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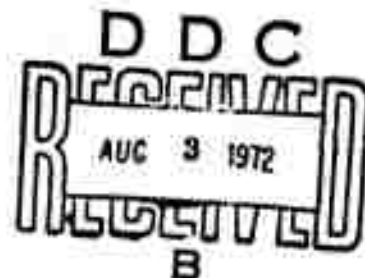
ANOMALOUS WATER

Final Technical Report

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ii						

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by

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Prepared For

Department of the Army
U. S. Army Missile Command (ARPA)
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ABSTRACT

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I. INTRODUCTION

"Anomalous water" was the name given by Fedyakin¹ to the fluid which condenses inside fine capillaries in presence of undersaturated H₂O vapor. This material has been extensively investigated by Deryagin and his co-workers [see for example references (2), (3), and (29) for recent reviews]. From this work, it has been shown that anomalous water is a solution of a residue in H₂O. The residue solidifies at -40°C, distills at 300°C,² has a density of 1.4,⁴ has a refractive index of 1.48 to 1.50,⁵ has a molecular weight of 180 ± 50 ,⁶ and raises the surface tension of water when dissolved. It decomposes back to water on excessive heating.^{2, 3, 8} Some of these properties have been explored by Western workers, and specifically, the freezing behavior,⁹⁻¹¹ and the refractive index^{12, 13} have been verified.

In addition, the residue has been chemically analyzed¹³⁻¹⁵ and its infrared spectrum has been determined.^{13, 14, 16} In their work on the IR spectrum and the chemical analysis of the residue, Lippincott, et al.,¹³ found the virtual absence of all significant impurities except for variable amounts of Na (<0.5%) and obtained a "unique" infrared spectrum. They also reported on the Raman spectrum. From these data, they concluded that the residue is a polymer of water. In agreement with conclusions in the Russian literature,³ they called the material "polywater."

Rousseau and Porto¹⁴ undertook studies similar to those of Lippincott, et al. They confirmed the infrared spectrum, concluded that the Raman spectrum was in error, and found relatively large concentrations of inorganic salts in their samples. While the latter could not account for the infrared spectrum, it was inferred tentatively that "polywater" was unlikely to be a polymer of water. Subsequently,¹⁷ it was suggested that the "unique" infrared spectrum of "polywater" could be duplicated by trivalent formates and acetates (see also, ref 26). This model was not satisfactory, however, because trivalent ions are not found in the samples^{13, 14} and because of the difficulty of understanding how these unusual materials could have been introduced into the material. In further work,^{18, 19} it was suggested that the

infrared-active component of "polywater" derives from a human sweat aerosol present in the laboratory air which deposits on the surface of the glass. The infrared-active component was claimed to be sodium lactate.¹⁸ In support of this hypothesis were analytical data involving electronic spectra and mass spectra.²⁰ The former showed the presence of carboxylic acid groupings in US-prepared material; the latter indicated the presence of phospholipids in USSR-prepared material.

This conclusion that "polywater" is a conglomeration of inorganic and infrared-active organic compounds could not, in our view, account for all the reported properties of the material. For example, the surface tension of anomalous water,⁷ its decomposition properties,⁸ its volatility,^{2,3} and the reported absence of organic material in some samples²⁰ pose problems. In addition, some workers^{2,20-22} report forming the material under organic-free conditions.

It is clear then that a considerable controversy has existed over the possible identity of "polywater." The recent report¹⁷ that "polyheavywater" has a similar spectrum to "polywater" argues strongly against a polymerized water model. However, positive identification of what appears to be an interesting fluid has not been made. The difficulty in this regard relates to the very low and erratic yields of material which have been reported by the various workers. For example, Willis, et al.,⁹ report that 5 to 10% of their capillaries contained a product. Others^{14,15} have also reported poor and irreproducible material preparation. The only prior report of substantial material production was by Page, et al.,²³ who claimed that milligram-size quantities of "polywater" had been produced in large quartz tubing. Preliminary results with this material indicated, however, that it was highly contaminated, containing up to 12% C.

Our work on anomalous water has had two objectives:

1. To produce enough material to verify its chemical composition unequivocally,
2. If it was found to be a water polymer, to assess its role in interfacial aqueous phenomena and its possible technological usefulness.

In the course of this work, our direct activities have focussed on item 1.

This project has been carried out in conjunction with a Contract No. 14-01-0001-2259 with The Office of Saline Water (OSW) of the Department of the Interior. Much of the material characterization was done on that program. Specifically, infrared spectra (to compare with US-grown polywater), molecular weights (to

compare with Deryagin's material), thermal stabilities, comparisons with various organic species, and D_2O (to test Rousseau's sweat theory) were carried out on that program.²⁴ On the other hand, all the preparative methods were developed on this program. In addition, some crucial techniques were developed and used on this program. Thus, a distillation-decomposition method has been used extensively to try to pin down one of the last remaining properties of anomalous water reported by Deryagin which still suggested that it is a polymer of water (Section IV). Also, a technique for measuring the refractive index of our samples has been developed (Section IV) to make really rigorous comparisons with the Russian material.

In our early work on the ARPA program, we identified two features of the process which improve the yield of anomalous water:^{10, 25}

1. The presence of hydroxyls on the silica surface.
2. Thermal instability in the silica-water vapor system.

More recently,²⁷ we have shown that the crucial feature of the latter is the need for supersaturation during some part of the cycle. Taking account of these factors, we experienced a substantial improvement with respect to erratic yields, but the actual amounts of material produced were highly unsatisfactory ($< 0.1 \mu\text{g}/\text{capillary}$). Correspondingly, we were stimulated to seek alternative procedures to improve the reactivity of the glass surface.

In this regard, we achieved a major breakthrough: We have shown that the erratic yields can be avoided using flame-tapered quartz and Pyrex tubes (up to 23-mm i.d.).²⁸ All of these tubes reliably yield a product ($\sim 0.05 \mu\text{g}/\text{quartz tube}$). Investigations on the OSW program (molecular weight and infrared spectra) indicated very strongly that this material is identical to the "Water-II" of Deryagin^{2, 3} and to the "polywater" of American workers,^{13, 14}

As the result of our excellent preparation technology, it has been possible to investigate the properties of anomalous water in some detail and to separate out the effects of its different components. It is our belief, based on these data, following Rousseau, et al., that anomalous water is a conglomeration of (inorganic and organic compounds). We believe that most of the material is formed when hot glass is allowed to contact the atmosphere. The data presented show, we believe, that all the properties reported in the Russian literature are capable of conventional explanation, without invoking the presence of polymeric water.

It is appropriate here to summarize the work carried out on the OSW program,²⁴ some of which has led to the above conclusion.

1. Infrared Spectra

Infrared spectra of both quartz- and Pyrex- grown anomalous water indicate that it is similar to other US-grown "polywater," i.e., a major band is found at 1600 cm^{-1} with lesser bands at 1400 cm^{-1} (sometimes a doublet) and at about 1100 cm^{-1} . In addition, there is often evidence for C-H stretching at about 3000 cm^{-1} and for inorganic species such as $\text{B}_4\text{O}_7^{=}$, $\text{CO}_3^{=}$, and occasionally, SiO_2 .

2. Molecular Weight

The molecular weight was determined by application of Raoult's law using the isopiestic method. Quartz-grown and Pyrex-grown materials showed values of 231 ± 21 and 183 ± 35 , respectively, in good agreement with the Russian literature.

3. Thermal Stability

Both infrared and molecular weight determinations showed that the material can withstand heating in air at 300°C for periods in excess of a day, with only minor decomposition. The results substantially suggest that there is a single major component of the material.

4. Experiments with Heavywater

Infrared spectra, molecular weight determinations, and thermal stability studies showed that "polyheavywater" is identical with "polylightwater."

5. Comparisons with Biological Material

The thermal stability was greater than expected from studies of natural sweat or from its infrared-active component, sodium lactate. Some evidence was obtained, however, to show that extensive heating of natural sweat leads to a minor, very stable product with a similar infrared spectrum to that of polywater. Both materials showed a shift in their infrared spectra on acidification, which suggested that their major infrared-active components are carboxylate groups.

The conclusion from that work is then that the material produced in the basic cone preparation technique developed on this program is organic in nature and is probably identical with the Russian-grown material. In the present program, we

have sought to prove this latter similarity unequivocally. Data on refractive index and boiling point (Section IV) are, in our view, conclusive in this regard. Similarly, we have shown that the Russian distillation-decomposition experiments can be explained with the organic hypothesis. Furthermore, we have demonstrated that the claim in Deryagin's work that his material was produced under organic-free circumstances is not appropriate, since the organic substance produced on the surface of the glass when he pulled his tubes will survive the high temperature vacuum treatment which he claimed cleans the glass. These data are presented in Section III. Preparative methods, and their possible development for the mass production of the material, are discussed in Section II. The basic conclusion is that the cone method leads to the best yield of material, i.e., about a monolayer on the surface of the glass. All efforts to expand surface area to increase the total amount of product were unsuccessful. Based on our present understanding, that the material is produced by the interaction of hot glass with organic compounds in the atmosphere, we regard efforts to produce more than a monolayer of material as futile. The difficulty with trying to expand the glass surface area on which this monolayer is spread relates to the extended (some seconds) high-temperature (glass melting point) treatments which are necessary to form the product.

II. PREPARATIONS OF ANOMALOUS WATER ON VARIOUS SURFACES

Although the bulk of the preparative work has utilized quartz and Pyrex, much effort has continued on examining other substrates for the formation of anomalous water. This line of investigation was prompted mainly by the observation that yield of material is much greater for Pyrex than quartz, and it was hoped to improve yields by use of these glasses. Consequently, various soft glasses were tested as substrates.

Initial results with borosilicate glass (Corning 7052) and soda-lime glass (Corning 0080) were presented in our report of May 1971.²⁷ Both of these glasses produce essentially the same amount of product as Pyrex. Infrared spectra of the material from the soda-lime glass showed the usual anomalous water peaks and no sodium borate. The absorption in the region of 1400 cm^{-1} was reinforced by a carbonate peak which could be verified by its companion peak at 880 cm^{-1} . Three μg of 0.1N HCl was added to the sample to convert the carbonate to CO_2 gas. The resulting sample had a spectrum which more closely resembled that of anomalous water (Fig. 1). The presence of carbonate is best explained by the absorption of CO_2 from the atmosphere into a liquid condensate which must be basic in pH. Since the cone technique had been employed, there was undoubtedly some caustic material released from the bulk of the tubing when this tubing was melted into cones. The infrared spectrum of the borosilicate product resembled that of anomalous water but was considerably more ambiguous (Fig. 2).

Pursuing this line of approach further, we have used zirconia glass (Corning No. 7280, 15% ZrO_2 , 11% Na_2O , 73% SiO_2) to form cones. This glass was selected because it contains no borates. Although its high coefficient of expansion led to difficulties in drawing cones without shattering the tubing, enough cones were made to determine the yield and the IR spectrum of the product. The yields were similar to those found in the normal Pyrex cones, while the IR spectrum is almost identical to the classic anomalous water spectrum (Fig. 3). No borate was evident, as

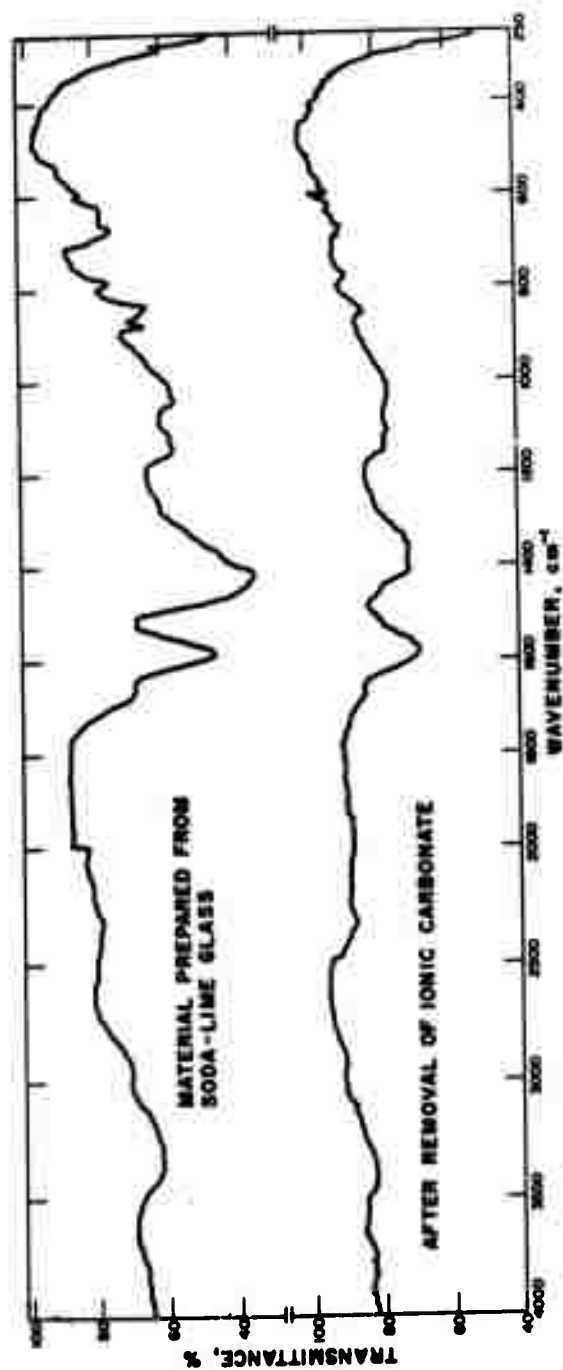


Fig. 1. IR spectrum of material produced from soda-lime glass cones

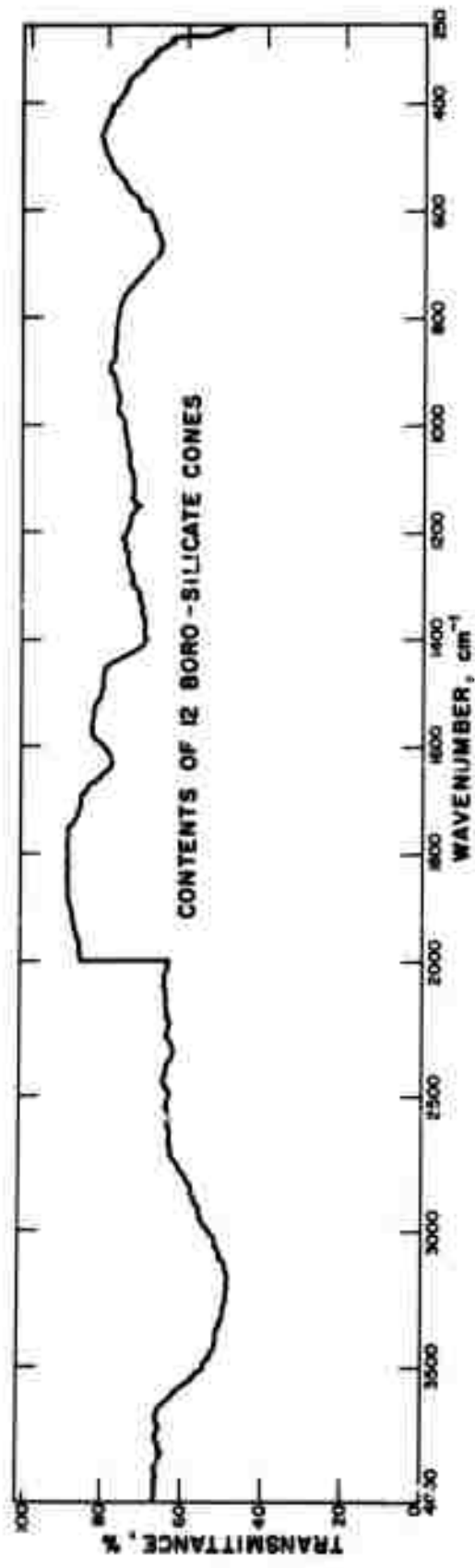


Fig. 2. IR spectrum of material from borosilicate glass cones

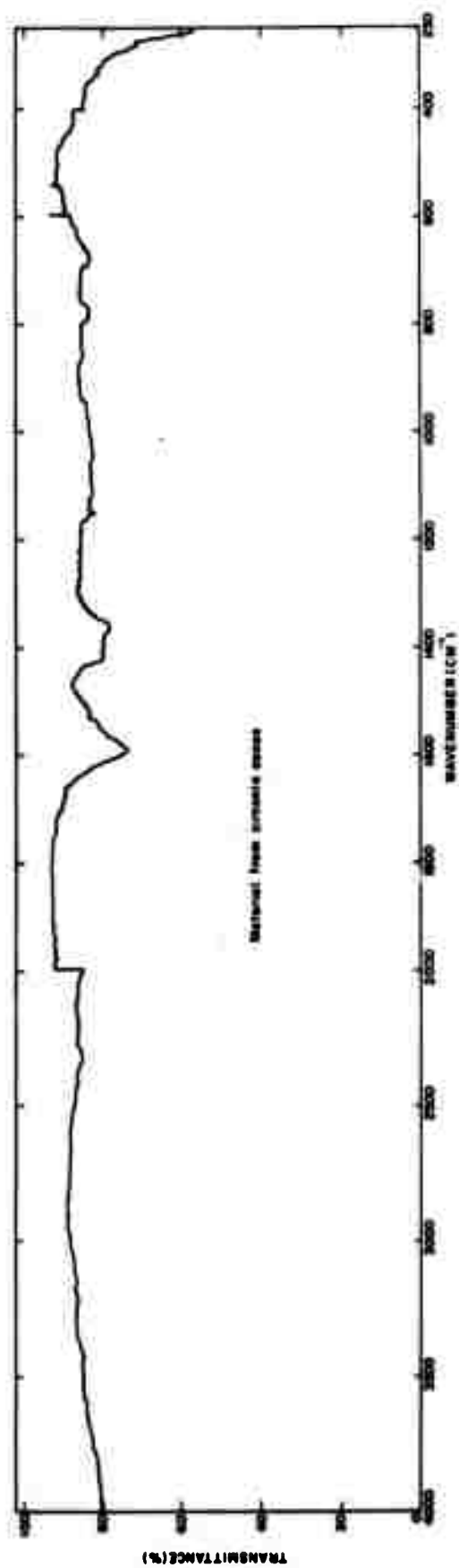


Fig. 3. IR spectrum of material from zirconia glass cones

expected. The material formed is probably of organic origin, since acidifying with 1 μl of 0.1N HCl caused the bulk of the spectrum to disappear. This is expected for an organic acid insofar as these acids are much more volatile than their salts. However, complete identification can only be made by observing the characteristic peak shift in the spectrum after acidification; this spectrum was too weak to allow this.

This was the only substrate to produce polywater which does not exhibit absorption peaks at 1100 cm^{-1} . This would indicate that absorption occurring at $\sim 1100\text{ cm}^{-1}$ is not attributable to polywater but to a different compound. This spectrum has been obtained repeatedly for zirconia-grown samples.

In general, infrared analysis is somewhat limited as to the extent of chemical identification possible. However, in some cases, positive identification has been made, e.g., $\text{CO}_3^{=}$ in the soda-lime preparation and $\text{B}_4\text{O}_7^{=}$ in some Pyrex-grown samples (refer to Fig. 14, ARPA Final Report, May 1971).²⁷ Additional information can also be inferred by comparing the IR spectra for zirconia-grown and quartz-grown material (Fig. 4). It is immediately obvious that the main difference is that there is considerable absorption in the 1100 cm^{-1} region for the quartz-grown sample. It would be difficult to attribute the contaminant in the quartz sample to the environment of the substrate during growth, since the preparative techniques were the same and both spectra have been reproduced many times. It is more likely that the source of contamination is the substrate itself and is therefore a silicate. This hypothesis is further substantiated by the fact that SiO_2 absorbs at $\sim 1100\text{ cm}^{-1}$ in the infrared. It is quite possible that the high temperature required to melt quartz into cones is responsible for the deposition of a small amount of silica powder onto the cone wall.

While this explanation as to the source of the 1100 cm^{-1} contaminant is only a postulate, it is felt that the lower melting zirconia glass is a more suitable substrate for the preparation of pure anomalous water. Using infrared analysis as a standard, it would appear that zirconia-grown material is the least contaminated of all tested, including those from substrates reported in our previous report.²⁷

It was hoped that such experiments would lead either to increased yield or to some understanding of why anomalous water is more readily produced on Pyrex than on quartz. Apparently the differences between Pyrex and quartz which affect the production of anomalous water are not influenced by the addition of more borates or the replacement of borates by soda-lime or ZrO_2 . This finding suggested that the

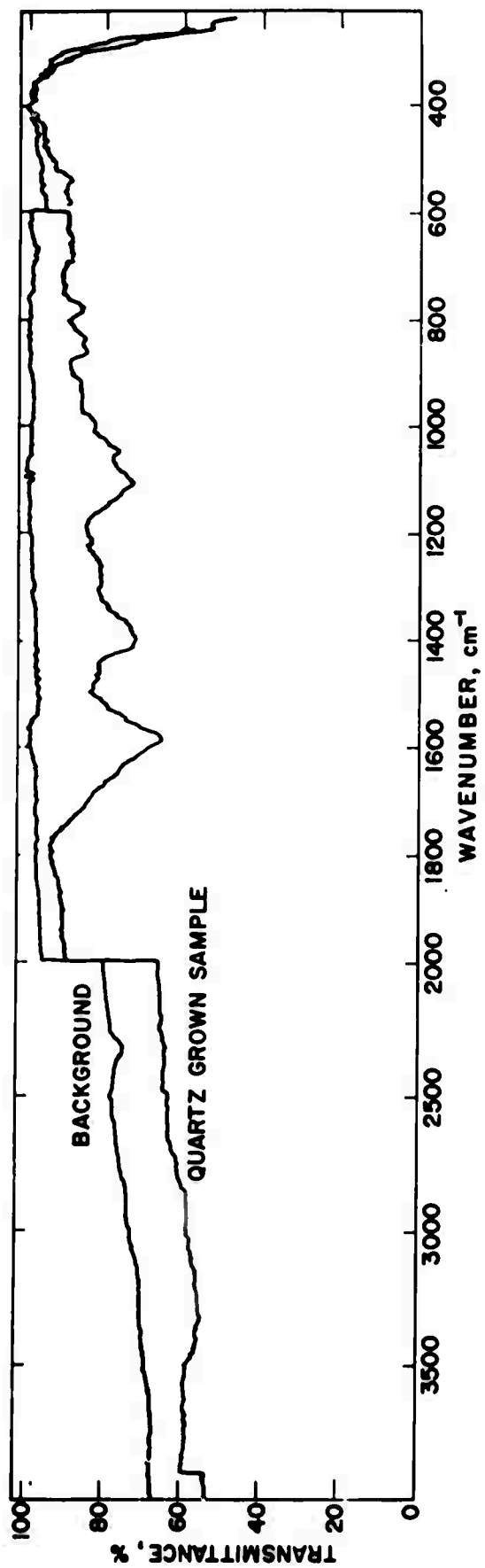


Fig. 4. IR spectrum of quartz-grown polywater

cone formation temperature may be the determining factor in the process. This formation process was then investigated as a function of temperature by heating zones on quartz tubes. Tubes heated for 1 min at temperatures between 600 and 800°C were exposed to water vapor in the usual way and examined for condensation. No condensation was formed either inside the heated zone or in the bands near the ends of the zone. It was therefore concluded that the hypothesis that anomalous water is formed as the result of the thermal gradients in the glass, either radial or longitudinal, is not correct.

Another experiment, which was also designed to investigate the effect of temperature on polywater formation, was performed whereby the Pyrex substrate was melted without the use of a flame. A 15-mm Pyrex tube, placed on a quartz plate, was heated at 1100°C for 1-1/2 hr and then air-cooled. After exposure in a desiccator, the product was collected and analyzed by infrared spectroscopy. The spectrum showed strong borate peaks but no anomalous water bands. The tube was then re-exposed. This time the product showed both borate and anomalous water peaks. This result is similar to that obtained from striped cones (see previous report),²⁷ and its interpretation is not clear. Whether anomalous water is formed initially and masked by large amounts of borate or whether the borate must be first removed to activate the surface for anomalous water formation was not clear. The former explanation seems more likely. In any event, it was decided to discontinue Pyrex activation by heating, since attempts to separate out the borates (e.g., by washing and/or distillation) were not successful and, therefore, the primary goal of the experiments, i.e., to determine whether anomalous water yields could be increased, was not achievable.

An experiment was carried out using zirconia cones which had been annealed at 627°C for 15 min and then cooled to 400°C in 25°C steps in 2 hr before oven-cooling. The yield of these cones was similar to that of the unannealed cones, in contrast to the yield in Pyrex cones, which is significantly reduced by annealing. This may be explained, in part, by the presence of borates in many Pyrex-grown samples and the relative lack of contaminants in zirconia-grown material. In other words, annealing Pyrex cones lowers the solubility of the glass, perhaps by conversion of tetraborate powder to fused B_2O_3 .

One experiment, suggested by Mr. Norman of Redstone Arsenal, was designed to explore the effect of having two glass surfaces in close proximity. A watchglass was placed on a Pyrex plate and the whole assembly exposed overnight in

a desiccator. Ideally, a ring of condensate would be found at a distance from the point of contact determined by the optimum separation for the production of product. What was found was a pool of liquid 0.8 cm in diameter. This diameter was determined by the amount of water absorbed by the polywater and therefore cannot be directly related to the optimum glass surface separation. The infrared spectrum of the material, although quite weak, displayed three peaks of roughly equal intensity at 1100, 1400, and 1600 cm^{-1} . Such a spectrum is more similar to the Battelle "blank"²³ than to anomalous water. The quantity of material produced was about 3 μg per watchglass.

We concluded from these experiments that the only promising approach to anomalous water production is the basic cone method, selecting a glass substrate which allows minimum contamination. It is our opinion that the cone method minimizes manipulation and handling of the glass, thereby reducing possible sources of contamination, as well as being efficient in terms of the amount of product per unit of labor.

III. EXPERIMENTS ON THE ORIGIN OF POLYWATER

A number of IR spectra have been determined for various samples of our polywater (many on the OSW program, but the results are directly relevant to much of the work carried out on this program), and they are quite similar to those reported by Lippincott, et al.,¹³ and Rousseau and Porto.¹⁴ Figs. 5a and 5b are examples obtained from quartz-grown and zirconia-grown materials, respectively, showing the characteristic peak at ~ 1600 and the doublet at ~ 1400 cm^{-1} . Absorption at ~ 1100 cm^{-1} (present in the quartz-grown sample) has also been observed by other workers and is believed to be due to ionic contaminating species. There can be little doubt, then, that many of our samples can reasonably be identified with the "polywater" of those workers. As Rousseau and his co-workers have pointed out, this spectrum is suspiciously like the spectrum of the salts of carboxylic acids; they believe that the IR-active species in polywater is organic in origin, deriving from a human sweat aerosol. Our own data support this general conclusion. The first indication that organic species were present in our material was from IR spectra showing C-H stretching bands at $2800\text{-}3000$ cm^{-1} ; see example in Fig. 5c. Since these bands are characteristically weak, detection is limited by instrumentation and concentration of samples. In our case, it was generally found that 20 to 30 μg of material was minimal for good resolution.

Also apparent in Fig. 5c is a shoulder at 1700 cm^{-1} , which is suggestive of a carboxylic acid, while the corresponding salt would absorb at ~ 1600 cm^{-1} . Verification of this assignment is quite straightforward since protonation of the COO^- group effects a peak shift from 1600 to 1700 cm^{-1} . This test was then applied to this and several other samples with the expected results. Fig. 5d shows an example of the shift observed with one of these polywater samples. These results are conclusive evidence that the major IR-active species present in these polywater samples are carboxylic acids and their salts.

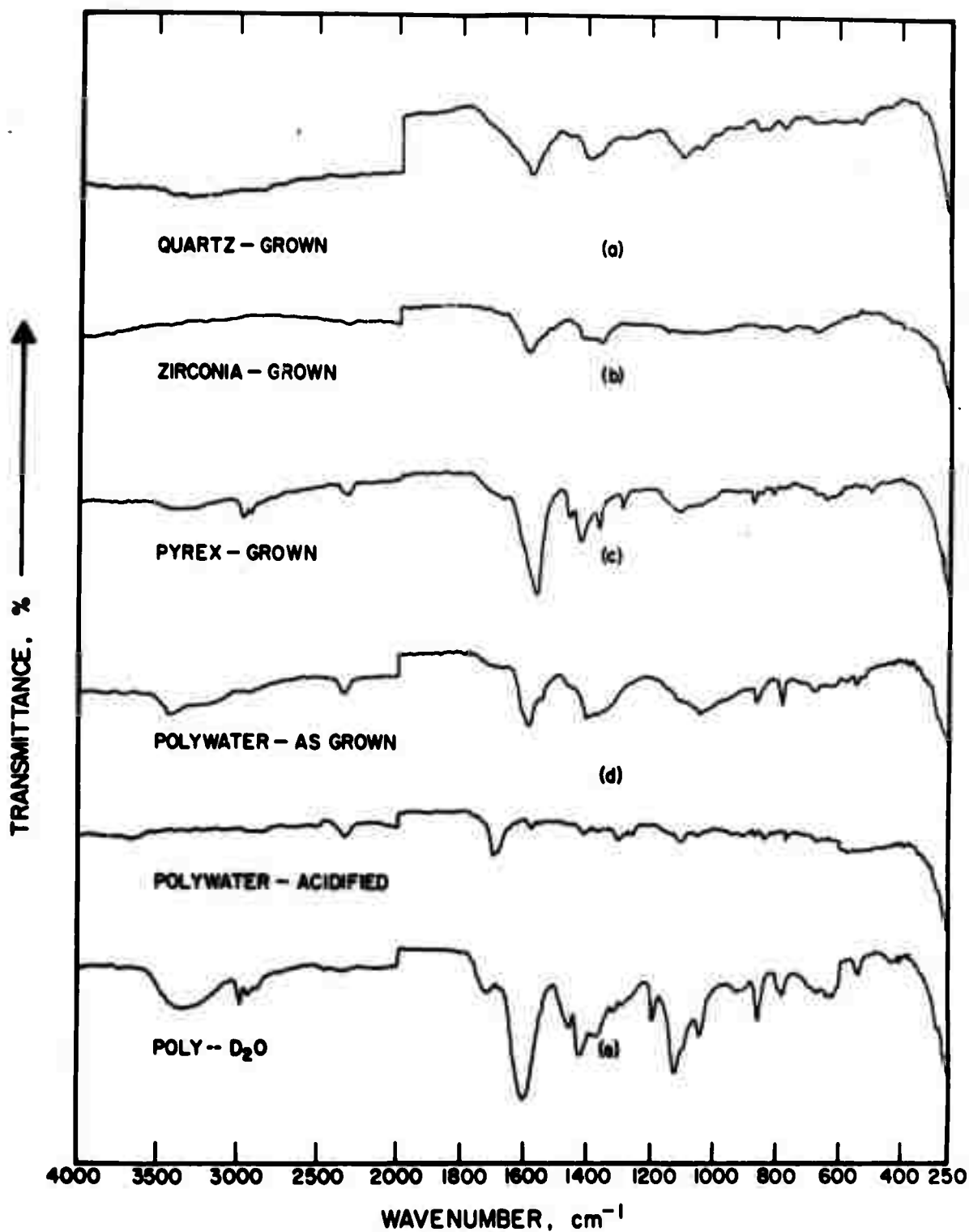


Fig. 5. Comparison of IR spectra for various polywater samples [(a) quartz-grown material; (b) zirconia-grown material; (c) polywater sample showing C-H stretching bands; (d) polywater sample showing the carboxylic acid shift; (e) poly D_2O grown on Pyrex in dry N_2]

Additional evidence in support of this identification of the IR active species was the results of experiments with D_2O . Poly- D_2O was prepared on Pyrex entirely in a dry N_2 atmosphere. After drying, the product was infrared analyzed. The spectrum (Fig. 5e) showed no shift for any absorption band attributable to polywater and, in fact, appears nearly identical to Fig. 5c, the spectrum for Pyrex-grown poly- H_2O .

This experiment showed that:

1. The major IR active components of polywater and "polyheavy-water" are identical.
2. This similarity cannot result from exchange between polyheavy-water and water to yield polywater.
3. The major IR active component of polywater cannot then be a polymer of water.

With overwhelming evidence that the IR active component of polywater was the salt of a carboxylic acid, the sweat theory, as an explanation for the phenomena, appeared not altogether illogical. In this theory, proposed by Rousseau, et al.,^{18,19} a sweat aerosol in the atmosphere condenses onto the glass surface to form a material responsible for the infrared spectrum of polywater. The infrared active component of sweat is apparently sodium lactate. One logical way of assessing the plausibility of this theory would be to find physical properties common to both polywater and sodium lactate (or sweat). Thermal stability studies made on the two compounds disclosed that, while the lactate was rapidly and completely decomposed by heat, sweat, on the other hand, exhibited significantly enhanced stability, more like that of polywater. This may be derived from noninfrared active contaminants present in the sweat which would stabilize lactate, or it may be that the stable component is some other carboxylate salt. In addition, it was observed that sweat char (water soluble portion remaining after heating in air at $300^\circ C$ for 24 hr) and polywater have similar IR spectra.

Consequently, we hypothesized that an organic aerosol, when coming in contact with the hot glass of the cone during pulling, does not experience complete combustion but rather decomposes to form the stable IR active component of polywater. Therefore it was proposed that if the interior of the tubing to be drawn into cones is not exposed to the atmosphere at any time during the coning process, the primary source of such organic contamination would be eliminated. Such an

experiment was performed and the details are as follows.

A long section of Pyrex tubing (sufficient for six cones) was cleaned with HNO_3 in the usual manner. Then, it was attached to a vacuum system in which only Teflon and glass were used between the tubing and a cold trap. After vacuum drying, the tube was back-flushed with purified oxygen and, while being flushed, it was baked in a furnace at 300°C for 2-3 hr. The furnace was then removed and the tube drawn into double cones with a $\text{C}_3\text{H}_8\text{-O}_2$ torch. After cooling, these double cones were cut in half and the resulting single cones exposed as usual. The yield was determined to be $1.2\ \mu\text{g}/\text{cone}$, which is somewhat lower than the yield from normal Pyrex cones (average $\sim 2\ \mu\text{g}/\text{cone}$).

Subsequently, the material was characterized by infrared analysis (Fig. 6). One immediately observes that the $1600\ \text{cm}^{-1}$ peak, usually present in polywater spectra, is entirely missing. It would appear, in this case, that the only IR-active component of the sample is tetraborate. Subsequently, the molecular weight was found to be 117. It is clear, then, that the material obtained from clean cones is not pure tetraborate (which shows an apparent MW of 75), but a molecular weight of 117 is considerably lower than that observed for any Pyrex-grown polywater (average 183 ± 35).

In order to confirm this unique IR spectrum and to avoid the possibility that the baking at 300°C was responsible for the different spectrum, a control experiment was performed. The original preparation was repeated, but with the difference that after baking in O_2 at 300°C the tube was cooled and then exposed to the atmosphere. It was left exposed while being flamed into cones. These cones were then exposed to water vapor, exactly as usual, and the material infrared analyzed. The spectrum showed typical polywater peaks with a strong absorption band at $1600\ \text{cm}^{-1}$. There can be no doubt then that the source of this peak is the atmosphere.

We feel that this is strong evidence in support of the theory that the source of polywater (or at least its infrared active component) is the result of the decomposition of airborne organics on hot glass.

A complementary experiment to the above was carried out under the OSW program and involved deliberately contaminating Pyrex cones with sweat. After a set of Pyrex cones was prepared, $10\text{-}20\ \mu\text{l}$ of a solution of sweat was placed in each cone and the cones were then "reflamed." The normal coning procedure involves reflaming them after their original drawing to reshape the cone. The approximate temperature achieved during this procedure is 1100°C , which is sufficient for

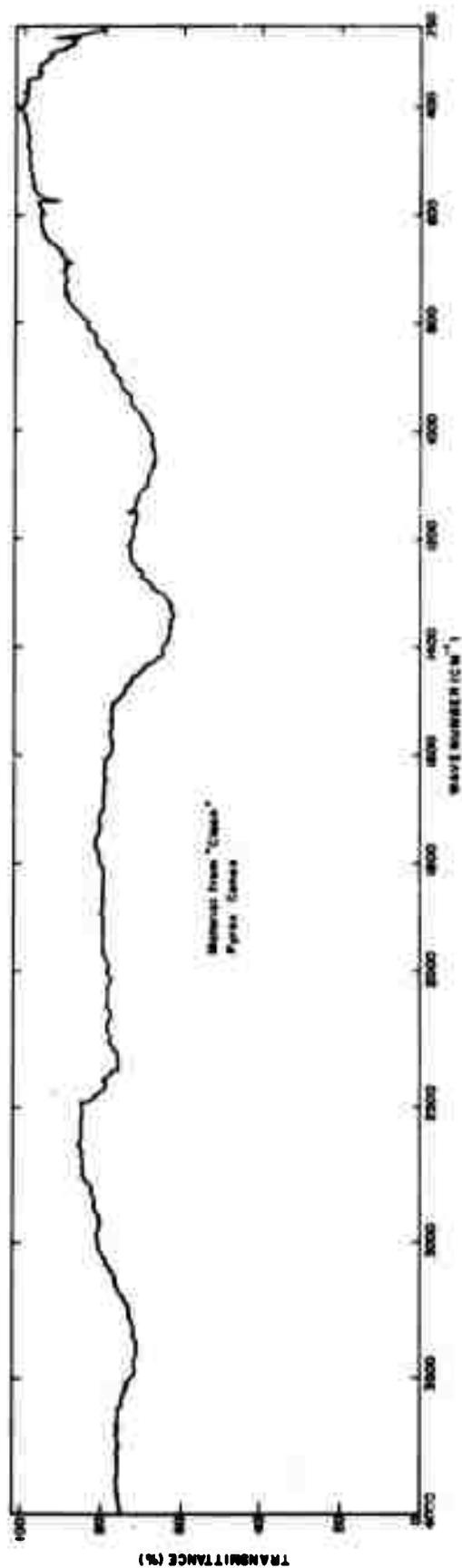


Fig. 6. IR spectrum of material from clean Pyrex cones

softening and working Pyrex and which is also far in excess of the temperature required to decompose sodium lactate. The cones were allowed to cool and then immediately extracted with liquid H_2O . The aim here was to eliminate the glass-water vapor interactions which have been postulated to be the primary driving force for the formation of polywater. The extraction was accomplished by placing ~ 0.5 ml of distilled water directly into the cone tip, siphoning it out, placing it into the next cone, and so forth. In this way, it was felt that the material extracted would be restricted to the decomposition product of the sweat during the reflowing of the cones. After completing the extraction, an aliquot of the solution ($\sim 1\%$ of the total volume) was mounted on an AgBr plate and allowed to desiccate for infrared analysis.

Fig. 7a shows the resultant spectrum. No attempt had been made to separate out salts from the sweat solution, which were undoubtedly present in substantial concentrations. The IR spectrum reflects these with very strong ionic sulfate peaks at 1100 and 620 cm^{-1} . Also evident in this spectrum are peaks at 1630 and 1400 cm^{-1} which, while typifying polywater, are in this case due to the decomposition product of the sweat. The presence of a carbonate, which absorbs at 1430 cm^{-1} , is highly improbable since there is no indication of its companion peak at 880 cm^{-1} .

These results are quite significant since they clearly demonstrate that an organic contaminant (such as sweat), once introduced into a hot glass surface, does not necessarily experience complete combustion, but rather may decompose to a compound which is still infrared active. This experiment was repeated for the purpose of extending it to include a distillation of the extracted material. If, in fact, there is a distillation product, a comparison of its IR spectrum with those of other polywater distillates could be helpful in assigning an identity to the material. Distillation would also serve to separate the organic constituents from the inorganic salts which are present in heavy concentrations in sweat.

The technique employed for the distillation is described in detail in Section IV. It is sufficient to say here that the material was distilled under vacuum at 300°C . A yellow oil was obtained which was not soluble in water. Polywater usually gave a water soluble distillate and this difference argues against a close relationship to polywater. The distillate was dissolved in a mixture of $75\%\text{ H}_2\text{O}$ - $25\%\text{ C}_2\text{H}_5\text{OH}$ of sweat and mounted on AgBr for infrared analysis. The spectrum proved to be quite similar to that of the material prior to distillation (Fig. 7b), with the exception that the 1100 cm^{-1} and 620 cm^{-1} peaks are now absent. This was

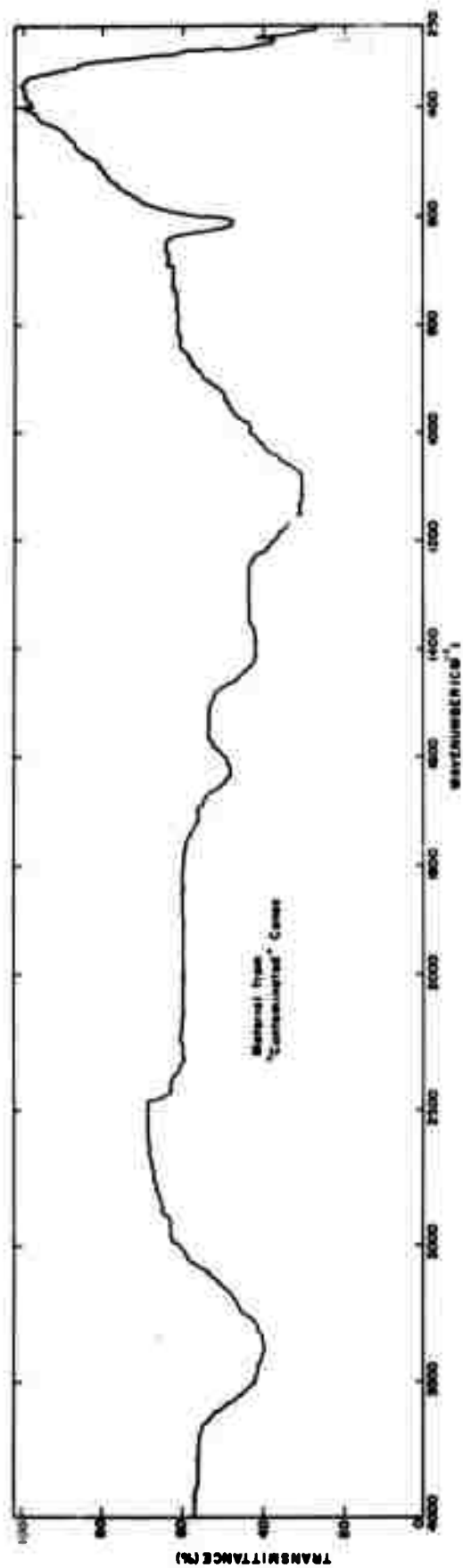


Fig. 7a. IR spectrum of material from sweat contaminated cones

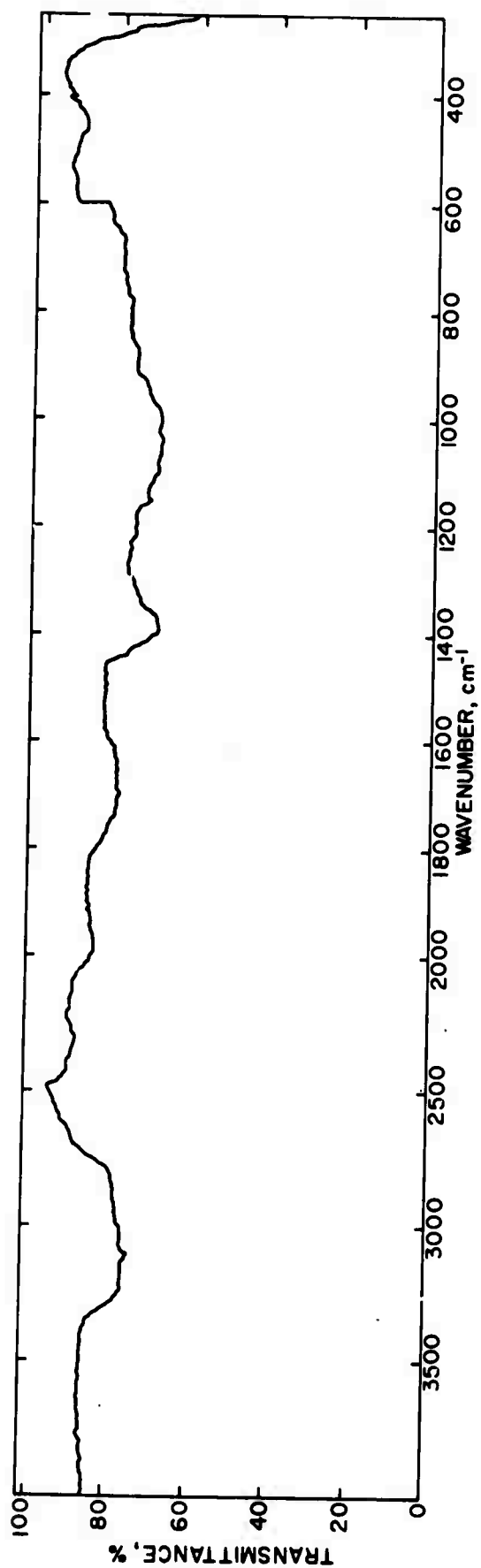


Fig. 7b. IR spectrum of material obtained by distilling material from sweat contaminated cones

anticipated since $\text{SO}_4^{=}$ was not expected to distill under these conditions.

These results indicate that it is possible to obtain an IR spectrum which is a reasonable facsimile of that of polywater from the partial decomposition of a common biological material, i.e., sweat. The observation that the sweat distillate is a yellow oil, however, led us to conclude that while there may be a relationship, the two materials are not exactly the same.

In another set of experiments, we have sought to explore the sweat theory of the origin of anomalous water by washing out drawn Pyrex cones and comparing the amount of the "blank" with the amount of material formed in a normal, high-humidity exposure. For this purpose, fresh Pyrex cones were filled with distilled water and left in a desiccator for 2 days. The water was then evaporated by vacuum so that the residue remained in the cones. The cones were then re-exposed for 1 hr and the product collected. The material gave a spectrum more similar to Battelle's "blank"²³ than to the usual Pyrex-formed anomalous water spectrum (Fig. 8), although the quantity of material formed in each case was the same as that produced using the usual technique ($\sim 2 \mu\text{g}/15\text{-mm-o.d. cone}$).

Evidently the small volume of condensed water formed in the normal anomalous water production procedure reacts differently with the glass than does a large volume of liquid water. This could result from extraction of material from the glass. It is claimed in the Russian literature that no comparable product to anomalous water can be leached from glass capillaries.³⁰ Our present data indicate that they ought to have seen material, which they would have found difficult to distinguish from their main material of interest. The different temperature-time relations achieved in cooling their fine capillaries after pulling them might be an important difference here, however.

The result of the deliberately contaminated cone experiment (i.e., incomplete combustion at 1100°C) is also of interest in view of the claim by Deryagin, et al., that organic-free polywater can be prepared from quartz which has been baked in vacuum at 400°C for 48 hr.^{2, 29} We thought that this heat-formed organic surface layer on the glass might survive this stringent baking procedure and thus invalidate his conclusion that polywater can be formed under organic-free conditions. The following preparation was carried out with quartz cones. A quartz vessel large enough to contain 40 cones of $1/2$ in. i.d. was made and baked at 600°C for 16 hr while being pumped continuously at <1 mm Hg. Freshly made quartz cones were placed in this vessel and baked at 400°C for 48 hr, also with continuous pumping.

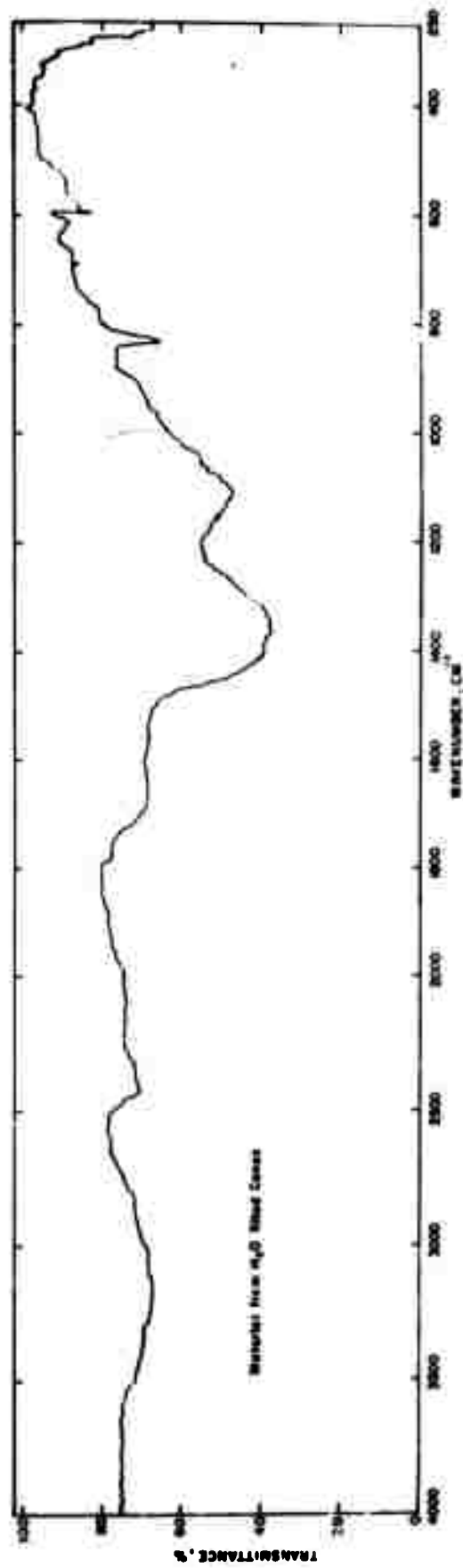


Fig. 8. IR spectrum of material from water filled cones

The cones were cooled while still under vacuum and then exposed to H₂O vapor in the normal fashion.

A typical amount of condensate formed, and was collected in the usual way. There was no significant difference between the IR spectrum of this material and that of normal polywater (Fig. 5a). The sample was then acidified to test for the presence of carboxyl groups. A very distinct shift from 1600 to 1700 cm⁻¹ was observed, thereby confirming that the major portion of the IR active material present was organic. It would appear, then, that the Russian claim is unsubstantiated and that some organic species, produced when the glass was originally pulled in air, can survive subsequent prolonged heating at 400°C under vacuum.

Prior to acidification, two aliquots of the sample were siphoned off for additional characterization. The first test was one of attempted decomposition at 600°C. According to Deryagin, et al.,^{2, 29} this leads to the breakdown of polywater to normal water. The sample was siphoned into a quartz capillary, desiccated, and evacuated to <1 mm Hg, and the capillary was then flame-sealed. This capillary was placed in a furnace at 600°C. A condensate, which was barely detectable, appeared as small, yellow droplets. The residue, on the other hand, represented the major portion of the sample and was a black char. The absence of any water condensate is also a strong indication that the sample was not composed of spurious organic contamination masking a significant component of polymerized water. The second aliquot had been siphoned into a quartz capillary for an index of refraction measurement (method discussed in Section IV). Two separate determinations were made at different dilution factors and the results were then used to calculate the index of refraction at zero dilution. The values obtained were 1.53 and 1.50, which are in excellent agreement with values reported by the Russians for "maximally modified water."

We feel that it is no mere coincidence that our material, while proven to be nearly all organic, has the same refractive index as Russian material which is claimed to be nearly organic-free. It should be clear, too, that our preparative technique disproves their assertion of organic-free preparations.

One point in the interpretation of the baked quartz preparation remained to be elucidated; namely, that the organic material which was extracted could have been introduced after the baking procedure. This was unlikely in view of our earlier reported results with Pyrex (c.f., Fig. 6) but a control experiment was carried out using quartz cones which were formed out of contact with atmosphere (as described above). If cones which were formed in this manner and subsequently baked under

vacuum at 400°C for 48 hr produced organic-free material, it would prove two things:

1. That the source of polywater (defined by IR activity) is the atmosphere, itself, in contact with the hot glass.
2. That the material thus formed has sufficient thermal stability to withstand 400°C heating under vacuum.

The experiment was run, and the IR spectrum of the resultant material is shown in Fig. 9b. The number of cones used for both experiments was the same. It is quite evident from Fig. 9b that the bulk of the material represented there is most likely SiO_2 and not organic. This bears out our original supposition that in the baked quartz cone experiment, the organic material extracted could not have been introduced after the baking procedure. This material, Fig. 9a, on the other hand, is not only of much greater quantity but was also verified to be largely made up of carboxylic acids. The peaks at 1100 cm^{-1} and 450 cm^{-1} in both spectra are believed to be due to SiO_2 .

The results of these two experiments provide conclusive evidence, not only as to the mechanism for the formation of polywater but also as to its general composition.

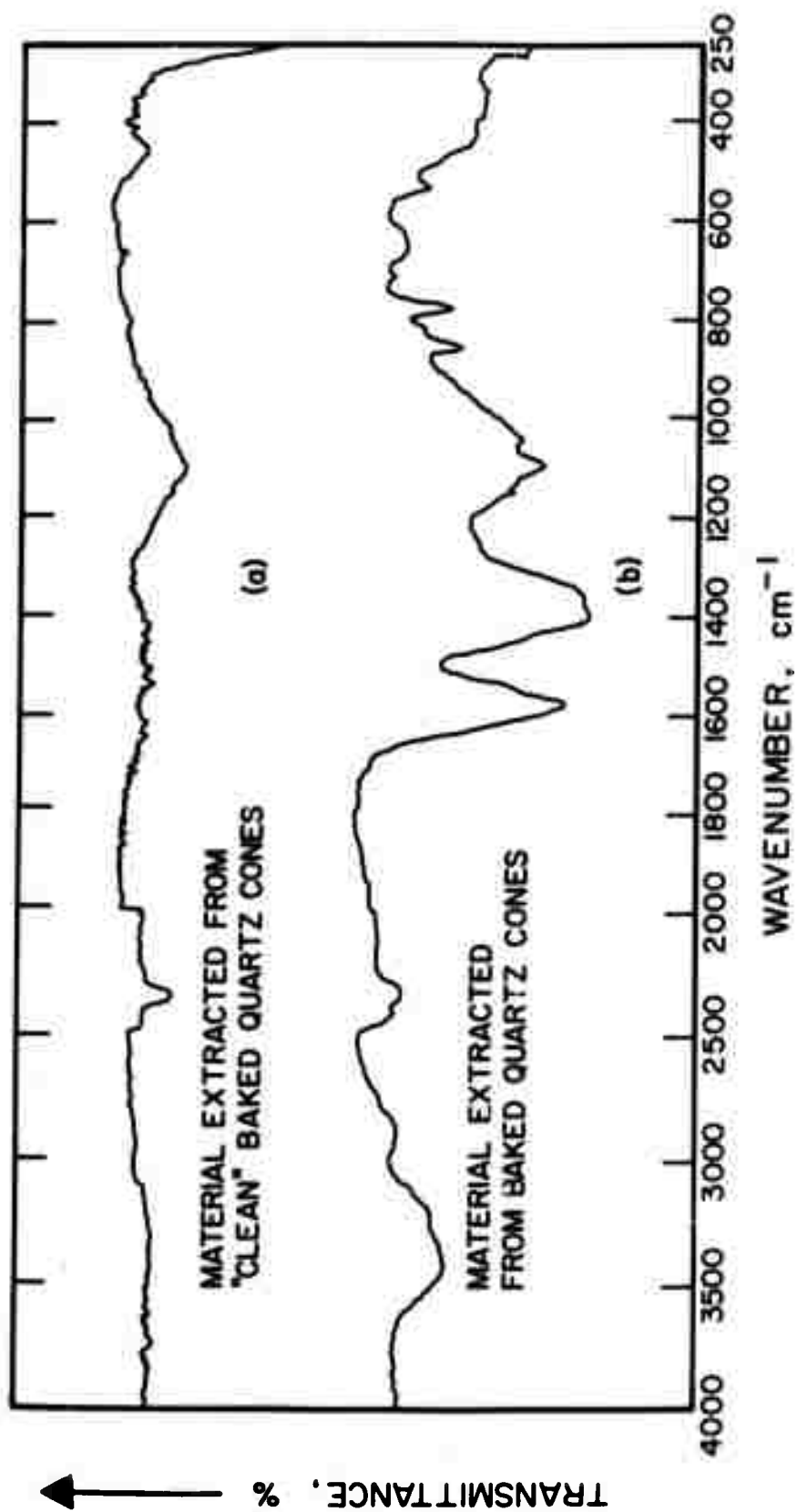


Fig. 9. IR spectrum of polywater grown in: (a) "clean" baked quartz cones; (b) baked quartz cones

IV. PHYSICAL PROPERTIES OF POLYWATER

A. Refractive Index

Techniques for measuring the refractive index of microgram quantities of material were mastered. Our method is based on that described by Deryagin.⁵ Fig. 10 shows the apparatus. The light source at the focal point of the lens produces a parallel beam of light which impinges onto a capillary immersed in a fluid. Since the index of refraction of this liquid is matched to that of the capillary, the parallel beam of light is not bent by the capillary walls. However the contents of the capillary, which have a different index of refraction, act as a cylindrical lens and bring the light to focus at a focal line. This line is above the axis of the capillary if the sample index is greater than that of the container walls and below the axis if the index is less. In the cases of anomalous water, normal water, and air, the refractive indices are all smaller than that of the capillary. Therefore, these samples act as diverging lenses and the focal line is located below the capillary. A 32X microscope objective is used to view the capillary and the line images. An immersible objective was used to eliminate bending of the light beam as it passed from the immersion fluid into the air above it. By using a green filter, the chromatic aberration was reduced and the focus was made sharper.

The measurements were carried out with a sealed capillary, partially filled with the sample. The meniscus of the sample was placed in the center of the field so that one side of the field contained the sample-filled portion of the capillary while the other side contained the air-column portion. After the capillary itself was brought into focus, the stage was raised until the air column side displayed a bright line. The stage was then raised further until the sample side of the capillary was bright. By using the calibrated drum of the microscope stage focusing mechanism, the distance between the focal line of the sample and the focal line of the air could be measured. Fig. 11 shows the capillary with the air focal line in focus.

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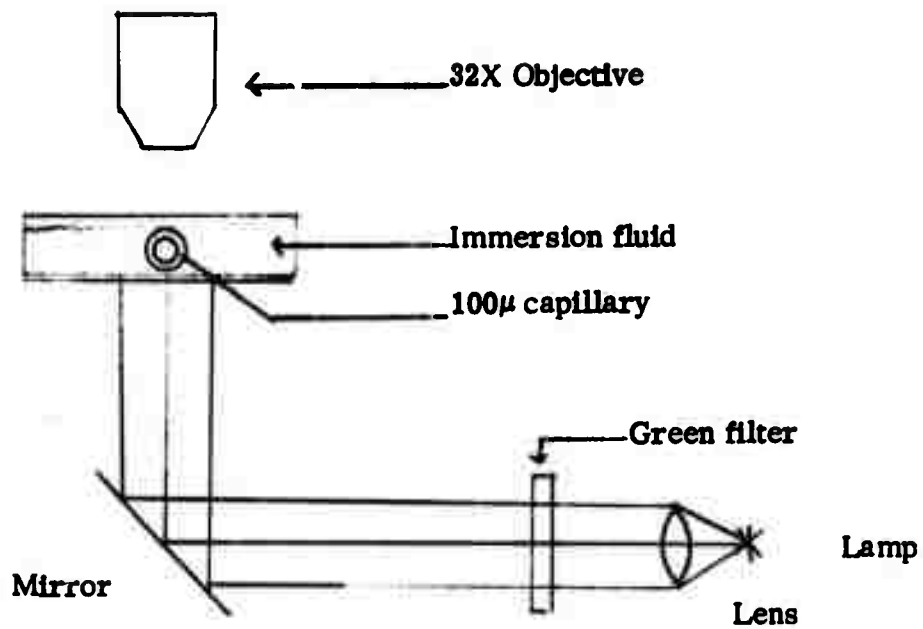


Fig. 10. Apparatus for measuring the refractive index of small samples

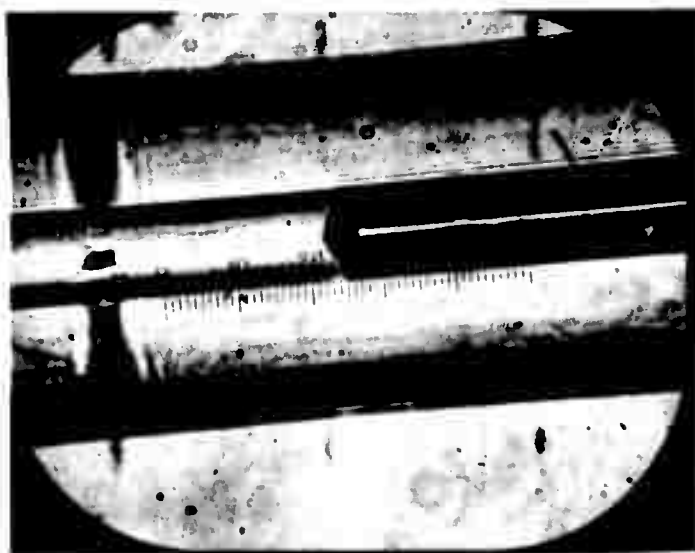


Fig. 11. Focal line of air in capillary acting as a cylindrical lens

This difference in focal length can be shown to be:⁵

$$\Delta f = f_{\text{air}} - f_{\text{sample}} = dn_c (n-1)/4 (n_c-1) (n-n_c) \quad (1)$$

where

d = capillary inner diameter,

n_c = index of refraction of capillary and the immersion oil, and

n = index of refraction of sample.

Although n can be calculated from this formula, it was felt to be advantageous, because of likely lens aberrations, to calibrate the measurement using solutions of known indices of refraction and to use these empirical data to determine the index of the sample.

This technique allowed us to observe $\Delta f/d$ values quite close to theoretical values, as is evident in Figs. 12 and 13. Fig. 13 shows the standard curve obtained using precision bore Pyrex capillaries, which have a variation in i.d. of only $\pm 2.5\%$, while Fig. 12 was obtained using hand-blown quartz capillaries, with a variation in i.d. of $\pm 10\%$. With refined diameter measuring techniques, a precision of 0.5% on the refractive index measurement can be obtained despite 30% variations in capillary size. This allowed us to calculate the refractive index of undiluted anomalous water to within 0.01 .

The refractive index of pure anomalous water residue is difficult to measure directly. This is because the residue contains bubbles and scatters light so much that no focal line can be observed. Therefore, solutions of anomalous water were measured and the required result obtained by extrapolating to zero dilution. The standard method for such determination is as follows.³¹ The molar refraction R_{12} of a two-component solution is given by:

$$R_{12} = \frac{X_1 M_1 + X_2 M_2}{\rho} \cdot \frac{n^2 - 1}{n^2 + 2} \quad (2)$$

Here n is the refractive index of the solution, X_1 and M_1 the mole fractions and molecular weights of the constituents, and ρ the solution density. R_{12} is also known to be the sum of the contributions from each of the constituents:

$$R_{12} = X_1 R_1 + X_2 R_2, \quad (3)$$

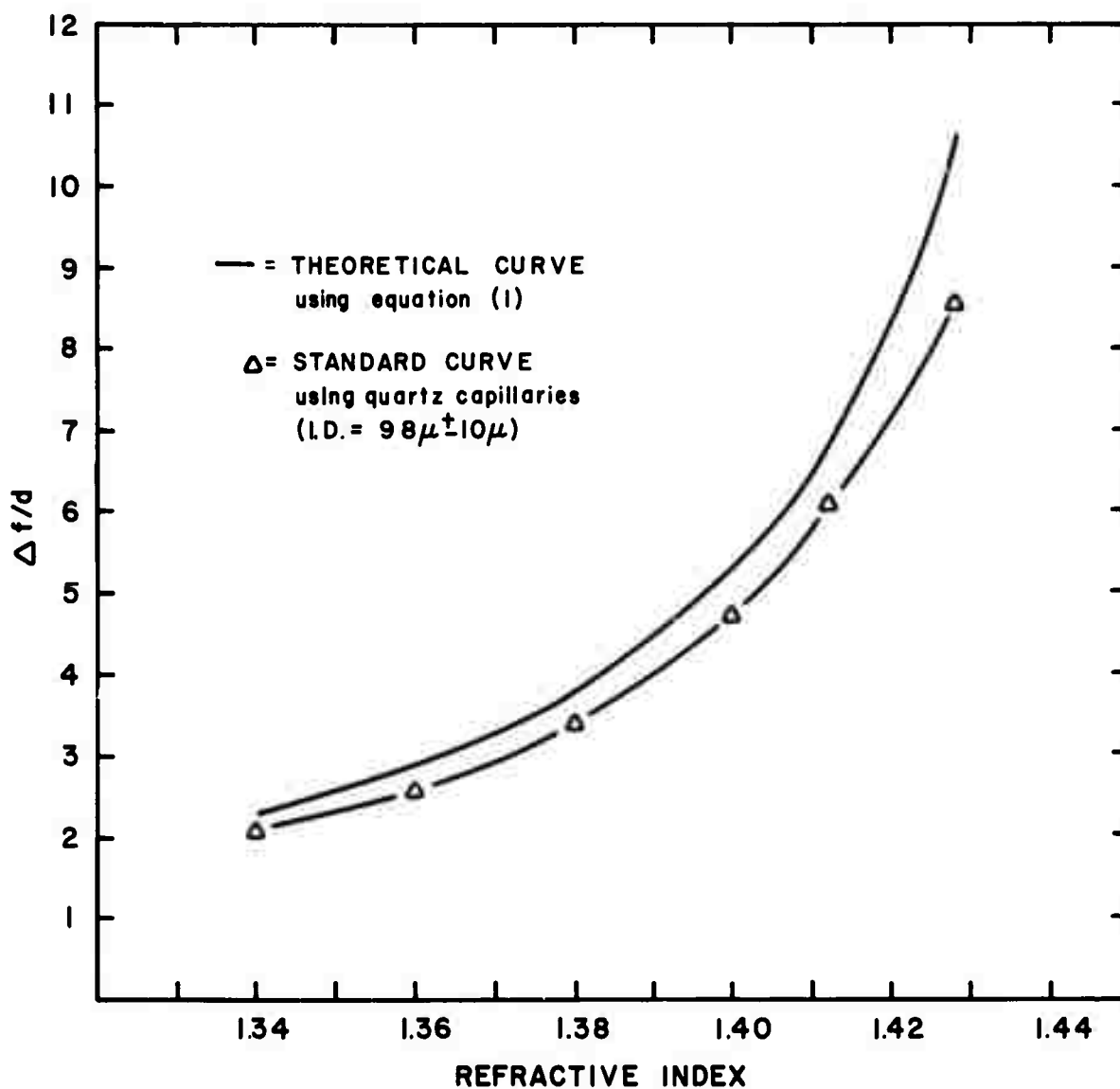


Fig. 12. Dependence of $\Delta f/d$ as a function of n obtained with a set of standard refractive index solutions in quartz capillaries

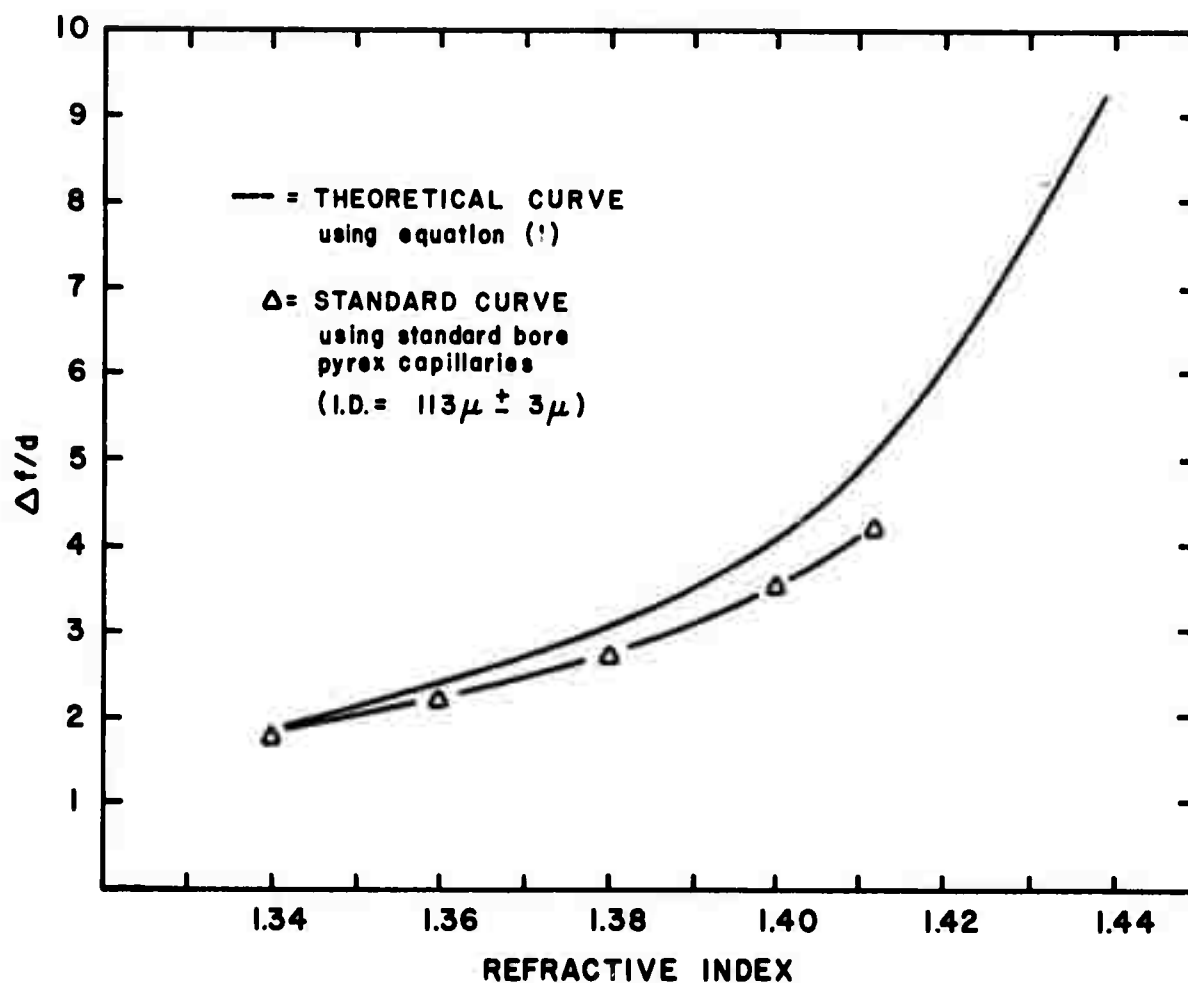


Fig. 13. Dependence of $\Delta f/d$ as a function of n obtained with a set of standard refractive index solutions in Pyrex capillaries

where

$$R_1 = \frac{n_1^2 - 1}{n_1^2 + 2} \cdot \frac{M_1}{\rho_1} \quad (4)$$

Then, we equate (2) and (3); we assume that for a column of polywater ℓ_o long in vacuum (with a density of 1.4) at humidity, r , such that its length ℓ is given by $\ell = r \cdot \ell_o$,

$$\rho = \frac{1.4 \ell_o + (\ell - \ell_o)}{\ell} = \frac{r + 0.4}{r}; \quad (5)$$

and we note that the mole fractions of the components are defined by

$$X_{H_2O} = \frac{\frac{\ell - \ell_o}{18}}{\frac{\ell - \ell_o}{18} + \frac{\ell_o (1.4)}{M_{pw}}} = \frac{r - 1}{(r-1) + \frac{25.2}{M_{pw}}} \quad (6a)$$

and

$$X_{pw} = \frac{\frac{25.2}{M_{pw}}}{(r - 1) + \frac{25.2}{M_{pw}}} \quad (6b)$$

Then, since $n_{H_2O} = 1.33$, we obtain the expression

$$\frac{n_{pw}^2 - 1}{n_{pw}^2 + 2} = \frac{n^2 - 1}{n^2 + 2} + 0.206. \quad (7)$$

Thus, n_{pw} can be obtained from refraction measurements on any solution of known composition.

As a test of both the experimental technique and method of calculation, samples of NaCl solution and glycerin were prepared and the refractive indices measured. The validity of the system was proven with observed values within 0.3% for glycerin and 2% for NaCl.

It should be noted that the accuracy of these determinations relies heavily on the accuracy of the ℓ_o measurement. This measurement can be read to within

± 0.0001 in. However, it is important that the dry column to be measured be dense and compact; otherwise the error in the measurement would rise significantly. An equally important factor in this regard is the relative amount of material present in the capillary. For a sample with l_0 less than 0.002 in., the error in this reading could therefore be greater than 10%. This was undoubtedly reflected in the wide variation in the calculated values for refractive indices which were obtained in initial determinations. In later determinations, care was taken to avoid this source of error, and the results tabulated in Table I show that, with the exception of three points (1.40, 1.57, and 1.60), all the results are very close (1.49 ± 0.02).

The two Pyrex-grown samples were taken from a single large (1 mg) sample and show an average value of 1.47 ± 0.02 . This is somewhat lower than the average value for the four quartz-grown samples, which is 1.53 ± 0.04 . This difference may be due, in part, to the presence of tetraborates ($n = 1.447$) in Pyrex-grown material. Comparison between our results and those of the Russians (1.49 ± 0.01) indicate strongly that we are dealing with the same materials.

B. Mass Spectra

In the hope of identifying some of the more stable organic components of polywater, mass spectroscopy experiments were carried out on various samples. These experiments were performed in collaboration with Dr. David Dolphin of Harvard University.

Samples were placed on a ceramic holder, previously flamed clean, which was placed in the spectrometer. The chamber was then pumped to 10^{-9} mm of Hg. In order to obtain greater peak heights, several (up to five) aliquots of material were deposited onto the holder, with rough pumping between each to evacuate the material to dryness.

The first set of measurements was made at temperatures ranging between 220 and 350°C using as-grown Pyrex material taken from a 1-mg sample previously amassed. The results of the measurement at the various temperatures are shown in Table II. The largest peaks at the lowest temperature (220°C) were at 60 and 149 mass numbers [the peaks at 28 (N_2) and 44 (CO_2) were also present in the blank]. As the temperature was raised, the peak at 149 disappeared (above 270°C), while the peak at 60 continued to increase in size until 305°C. This may indicate that the latter is a decomposition product of the former. At higher temperatures, we begin to see a peak at 207. Other peaks at 85 and 139 also appear at elevated temperatures, in addition to more CO_2 and N_2 than can be explained by what was

Table I. Refractive Index Determinations

<u>No.</u>	<u>Sample</u>	<u>ℓ_0</u>	<u>r</u>	<u>$\Delta f/d$</u>	<u>n</u>	<u>n at zero dilution</u>
1	Pyrex-grown	0.0067	6.28	2.115	1.356	1.48
		0.0067	9.94	1.892	1.344	1.44
		0.0067	17.015	1.791	1.337	1.40
		0.0067	9.015	1.991	1.351	1.50
2	Pyrex-grown	0.0090	6.66	2.125	1.357	1.50
		0.0090	10.53	2.018	1.345	1.46
		0.0090	16.53	1.881	1.343	1.49
		0.0090	7.14	2.009	1.351	1.47
						1.47 \pm 0.02
1	Quartz-grown	0.0025	15.48	1.875	1.343	1.49
		0.0025	7.28	2.369	1.368	1.60
2	Quartz-grown	0.0032	18.31	1.920	1.345	1.57
3	Quartz-grown	0.0035	17.46	1.874	1.342	1.50
4	Quartz-grown "baked"	0.0063	6.48	2.685	1.363	1.53
		0.0063	5.94	2.613	1.360	1.50
						1.53 \pm 0.04

Table II. Peak Heights for Samples Taken from Pyrex 1-mg Preparation

Sample	Temperature of Sample	Mass Number							
		29 (28)	45 (44)	60	69	85	139	149	207
Blank	220	1.0	1.6	0.8	5.8	0.7	-	0.5	-
First Sample	220	0.6	1.2	2.0	1.7	0.3	-	1.0	-
	255	0.9	1.5	1.7	1.6	0.4	-	0.3	-
	270	4.9	5.8	6.8	1.7	0.9	0.4	0.4	0.5
Second Sample	305-320	10.5	7.4	6.2	3.3	3.7	2.6	-	0.9
	350	6.6	3.9	2.3	3.7	10.8	2.5	-	2.6
	220	1.2	3.4	2.2	3.3	0.7	-	6.4	-
Blank	280	1.6	2.2	2.2	2.7	2.2	1.1	0.35	0.5
	340	4.0	0.4	<0.3	1.2	4.6	-	-	1.9

found on the blank. However, it is not certain that these did not result from residual material from other experiments, which was not removed from the vacuum chamber of the instrument when cleaned.

The results for a second sample are also displayed in Table II. The results are comparable with those of the first sample. Both results indicate that the 149 MW species is volatile at lower temperatures, and it was decided that a second series of measurements should be made at temperatures below 200°C.

Table III shows the results of the second set of experiments. The Pyrex-grown sample was taken from the same source as in the previous experiment, namely, the 1-mg sample. The component with mass number 149 showed increasing peak height with temperature in the range used, 80°-125°C. An additional component was observed at mass number 73. In the previous experiments this peak was not monitored, since it was also quite strong in the background runs. As was expected, the 207 component was not observed at these lower temperatures.

A sample of zirconia-grown material, which shows no 1100 cm^{-1} band in its IR spectrum, was also tested (Table III). All the mass numbers observed with the Pyrex-grown polywater were observed with this sample, as well as one additional component occurring at mass number 87-88. This was a relatively strong peak with maximum height at about 280°C. The more prominent components are depicted in Fig. 14 in the form of peak height versus temperature.

The last sample to be tested was the 300°C fraction from the distillate of zirconia-grown material (distillation No. 7, see below). Since the sample size was small, the peaks were all somewhat weak. However, it should be noted that the components with lower mass number are of about equal intensity as the heavier components, whereas in the previous experiments the 45 (CO_2), 60, and 73 portions were much stronger than the 149 and 207 mass numbers. This would imply that this material is of highest molecular weight, and has greater stability than the original material. This conclusion would be consistent with its method of preparation.

We would conclude from these experiments that we are preparing essentially the same material on both Pyrex and zirconia glass and assume that the molecular weight of the material is that of the highest mass number observed, i.e. 207.* It is also apparent that none of the prominent mass numbers observed could be caused by

* This is in reasonable agreement with our previous estimate²⁴ for the MW of ~230. It would imply that the density value (1.4) used in that calculation is too high; based on these data, a value of ~1.26 would appear more appropriate.

Table III. Peak Heights for Three Samples

Sample	Temperature of Sample Probe, °C	Mass Number							
		45	60	73	87	88	139	149	207
Blank	60	—	—	—	—	—	—	—	—
Background	70	2.8	0.6	0.7	—	—	0.7	1.0	—
Pyrex	80	4.0	2.4	1.4	—	—	1.8	1.4	—
Pyrex	125	~ 4.8	3.1	1.5	—	—	1.7	1.7	—
Background	125	1.8	0.9	0.8	—	—	1.0	0.8	—
Background	40	~ 12	0.9	—	—	—	—	0.4	—
Zirconia	110	~ 4.8	2.9	—	—	—	1.5	1.4	—
Zirconia	175	~ 5.6	4.5	—	—	—	1.2	1.5	—
Zirconia	235	~ 8	~ 6.4	~ 4.8	4.0	~ 4.5	0.9	2.5	0.9
Zirconia	260	~ 10.4	~ 10.4	~ 6.4	~ 6.4	~ 4.8	1.1	1.1	1.4
Background	275	3.3	1.7	—	—	—	1.3	0.8	—
Zirconia	280	~ 10.4	~ 12.8	~ 8	~ 5.6	~ 5.2	1.4	1.2	2.6
Zirconia	290	~ 8	~ 16	~ 8	3.1	3.2	1.7	1.0	2.0
Background	290	2.5	1.5	1.6	—	—	1.4	0.8	0.8
Zirconia 300° distillate	235	4	1.0	1.1	—	—	1.0	1.2	—
Zirconia 300° distillate	275	2	1.2	1.1	—	—	1.0	1.1	—
Zirconia 300° distillate	290	2.6	1.1	1.1	—	—	1.1	0.9	0.7

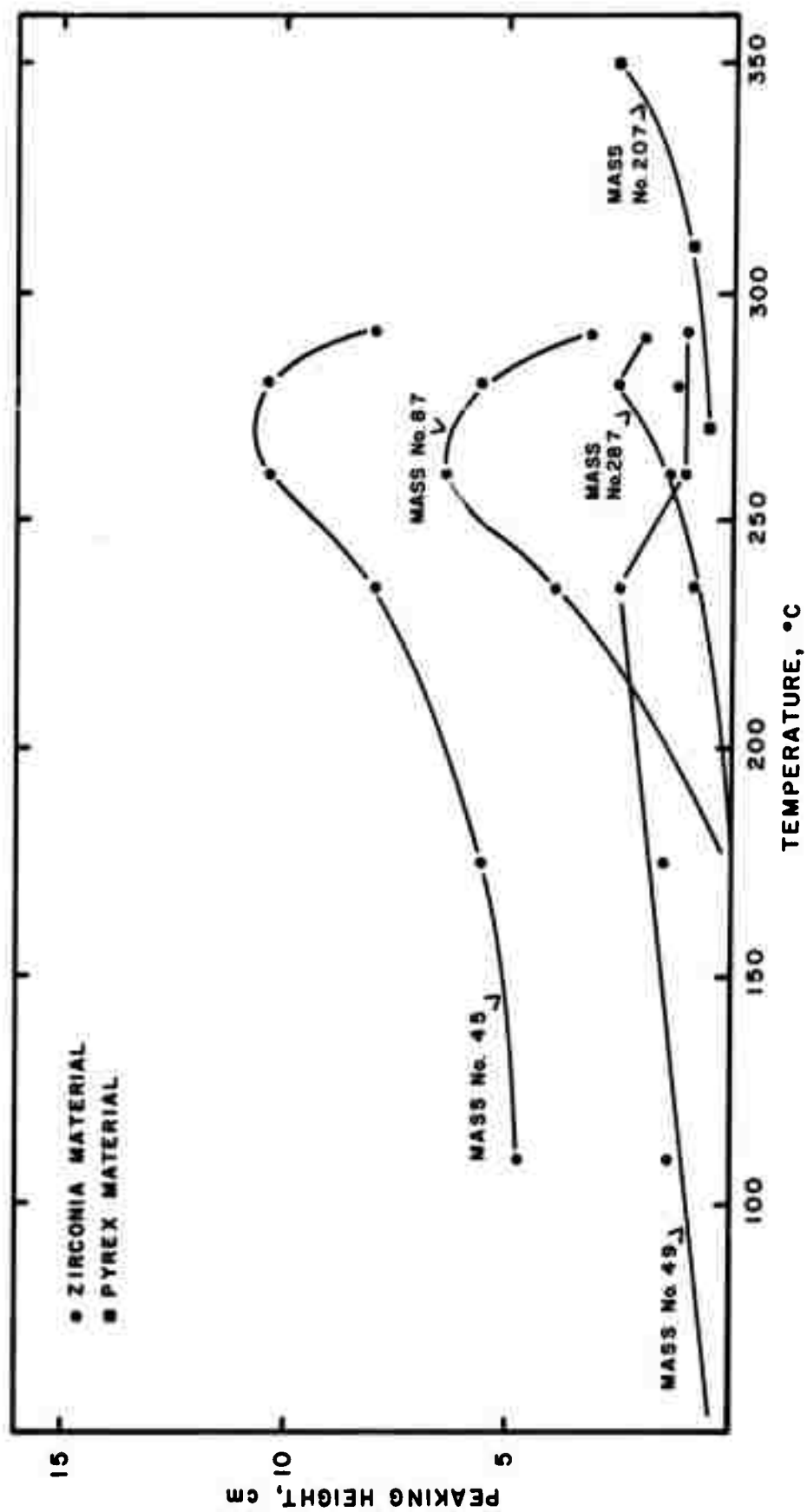


Fig. 14. Peak height versus temperature for various mass numbers

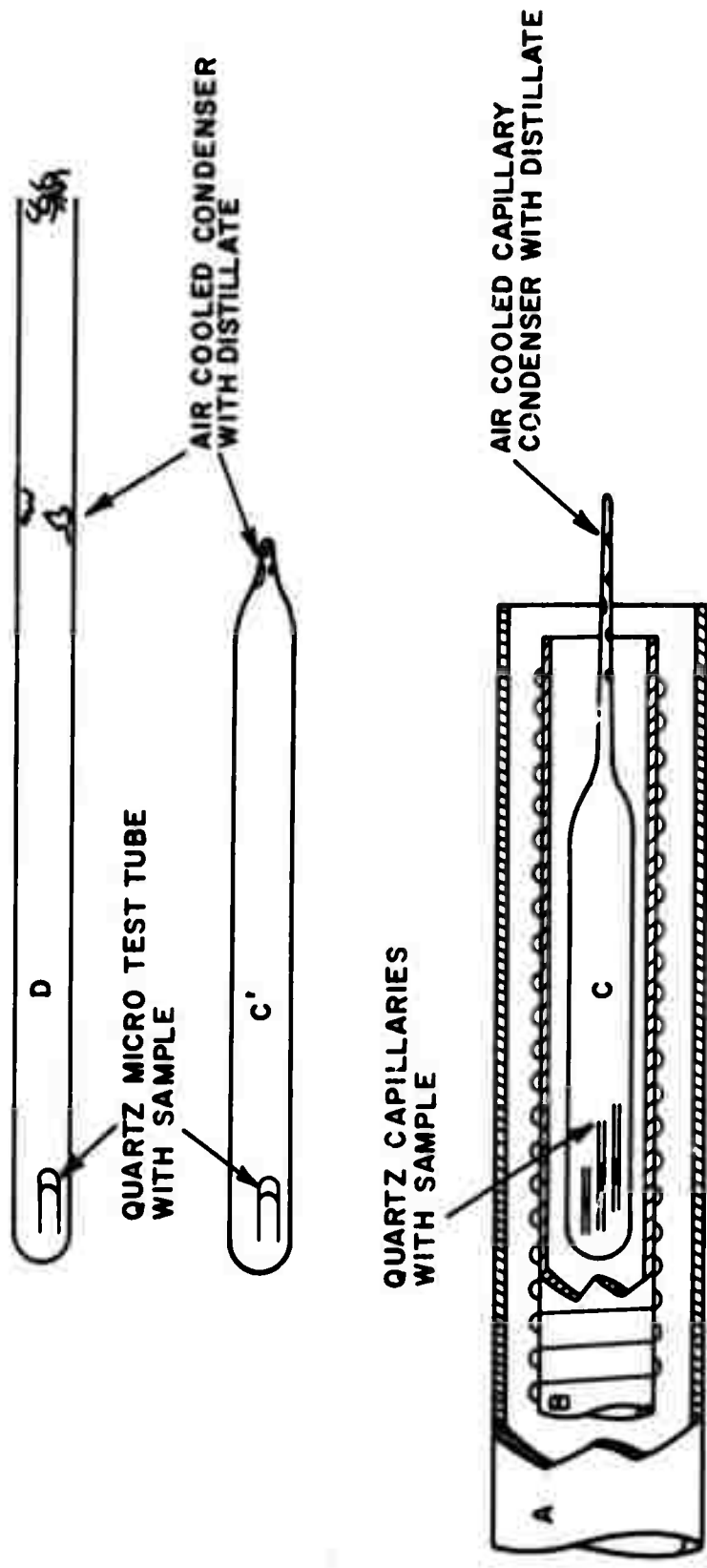
a polymeric form of water.

Interestingly, this ion has also been observed in high temperature mass spectrometric studies of anomalous water by DePaz, et al.³² They observed three ions (m/e 207, 208, 209) of relative abundance similar to that of natural Si. They assigned a structure of $H_{11}Si_3O_7$. Orlov,³³ on the other hand, attributes the peaks to the organo-silicon compound $(CH_3)_5Si_3O_3^+$. Regardless of the validity of either interpretation, all mass-spectrometric investigations (including those of V. L. Tal'roze²⁰) do concur on one point, namely, that there has been no evidence, to date, of a polymeric form of water.

C. Distillation of Polywater

The presence of some organic material in various polywater samples prepared in this laboratory has been confirmed by infrared analysis. Indeed, a substantial part of the work in the United States has focused on the infrared spectrum of polywater. The Russian work, on the other hand, has involved no IR analysis and consequently one could not fairly conclude that the two bodies of work are on the same material. The molecular weight and refractive index data referred to above made the similarity very likely, but we sought to measure the boiling point of our product, for comparison, and to carry out the very crucial decomposition experiment, whereby they showed conversion back to pure water.^{2,8,29} Also, it was possible that only a minor component of the material which we characteristically make is, in fact, responsible for the various physiochemical properties observed by the Russians. Consequently, the distillation of polywater became a pivotal experiment serving a dual purpose: (1) to link our data with that of the Russians, and (2) to purify our material.

The apparatus for distillation of polywater is shown schematically in Fig. 15. Quartz tube A (18-mm i.d.) serves to insulate the heating unit from drafts in the room and to keep the temperature constant. Tube B is a heating unit wound with Kanthal high resistance wire. The temperature (range from 50 to 800°C) of this unit is controlled by two variacs. The distillation chamber, C, is a sealed quartz tube (2.5-mm i.d., 5-mm o.d.) with one end drawn into capillary. This end is suspended outside the heating unit and serves as an air-cooled condenser. The samples to be distilled are placed in capillaries at the other end of the chamber. While being heated, the samples evaporate, escape from these capillaries, and settle at the cool end of the chamber. Tube C is a modified distillation chamber.



A. QUARTZ INSULATION TUBE, 18 m.m. i.d.

B. HEATING UNIT, 7 m.m. i.d.

C, C', D. DISTILLATION CHAMBER, 2.5 m.m. i.d., 5 m.m. o.d.

Fig. 15. Distillation apparatus

Here the capillary condenser was replaced by a cone so that any condensation at the tip of the cone could be recovered easily with a micropipet. In this case, the sample holder was a micro test tube, which was much more easily handled than the capillaries. Tube D was for distillation experiments being done at atmospheric pressure (e.g., $\text{Na}_2\text{B}_4\text{O}_7$).

In all, seven distillations of polywater, plus attempts to distill $\text{Na}_2\text{B}_4\text{O}_7$ and poly- D_2O were carried out. In addition, two polywater samples were distilled from acid. The results are summarized in the following:

• Distillation No. 1: A sample of polywater collected from Pyrex cones was transferred into capillaries, dried, and placed in distillation chamber C. The distillation chamber was evacuated (to about 0.5 mm Hg pressure) and sealed under vacuum. The sample was heated initially at 100°C , and no condensation was observed at the tip of the capillary condenser. The temperature was then increased gradually, while the distillation chamber was observed very carefully with the help of a microscope. No visible condensation was observed at 250°C or after 1 day at 300°C . However, a product distilled over at 300°C during the next 3 days. We purposely kept the temperature as low as possible to minimize decomposition. According to our observation, the solid-like starting material did not melt, but went into the gas phase directly and condensed at the cool end. Black solid materials, which did not distill, were left inside the capillary sample holders. Because of the minute amount of the distillate, no attempt was made to identify the product directly. As an indirect test, the distillation chamber was placed in an oven and was heated to 700°C overnight in order to see if the product would decompose to normal water, as reported by Deryagin.^{2, 3, 8, 29} The distillate disappeared after heating and the distillation chamber was again placed inside the heating unit and the distillation repeated. However, no condensation was observed. It seems that the decomposition product of the distillate must have reacted with the hot quartz and it was not possible to identify it.

• Distillation No. 2: This distillation was done with distillation chamber C. To remove organics, the distillation chamber was baked at 200°C in the presence of air for 2 hr and the sample (about $100\ \mu\text{g}$) was heated at 200°C in air for 2 hr before use. Otherwise, the procedure and handling were the same as described above. After 2 days at 300°C , some crystalline material was found at the tip of the cone. The distillation was completed after 5 days, i.e., there was no more increase in product formation. The chamber was opened and the distillate was exposed to water;

then the solution was transferred to an AgBr plate. While the IR spectrum of this product is weak (Fig. 16), it shows absorption at 1580, 1380, and 1080 cm^{-1} (characteristic of polywater) and a very weak band at 1700 cm^{-1} (characteristic of carboxylic acids). This sample was then deliquesced and transferred to a capillary tube and dried over P_2O_5 .

When the sample was completely dried, the capillary was cut and sealed at both ends and reserved for a decomposition experiment. For this purpose, the capillary was placed in the distillation apparatus directly at 600°C . One tip of the capillary was left outside the heating coil and, after 30 min of heating, a liquid condensate appeared at this cool end of the capillary. Condensation was complete in 4 hr.

The capillary with the decomposed product was placed into a freezing point determination cell and a control experiment was done with distilled water in a capillary tube. These two capillaries were placed side by side in the freezing cell. The cell was cooled down to -45°C with cold N_2 gas and the temperature was brought up slowly ($2^\circ\text{C}/\text{min}$) while the melting process of both samples was observed. The melting point for these samples was 0°C . The result of this experiment suggests that the decomposition product was water. This water was presumably the decomposition product of a polymer of water, a similar conclusion to that shown in the Russian work.²

In order to ensure that this liquid condensate could not have been water previously adsorbed on the capillary walls, two control experiments were performed:

1. A 6-cm capillary was dried over P_2O_5 and sealed at both ends. The decomposition procedure was then repeated as described above, but no liquid was found at the cold tip of this capillary.

2. Another 6-cm capillary was filled with water, dried over P_2O_5 , and sealed. After this capillary was heated at 600°C , no liquid condensate was observed.

One precaution which had not been taken in this preliminary experiment was to eliminate oxygen in the capillary by evacuation before sealing and heating at 600°C . If, in fact, the distillate were organic, then the presence of oxygen would have aided its oxidation to CO_2 and water. In any event, the decomposition experiment just described was not quantitative; there was a small amount of what may have been a char still remaining. A similar set of experiments was also carried out on other materials (distillation No. 5).

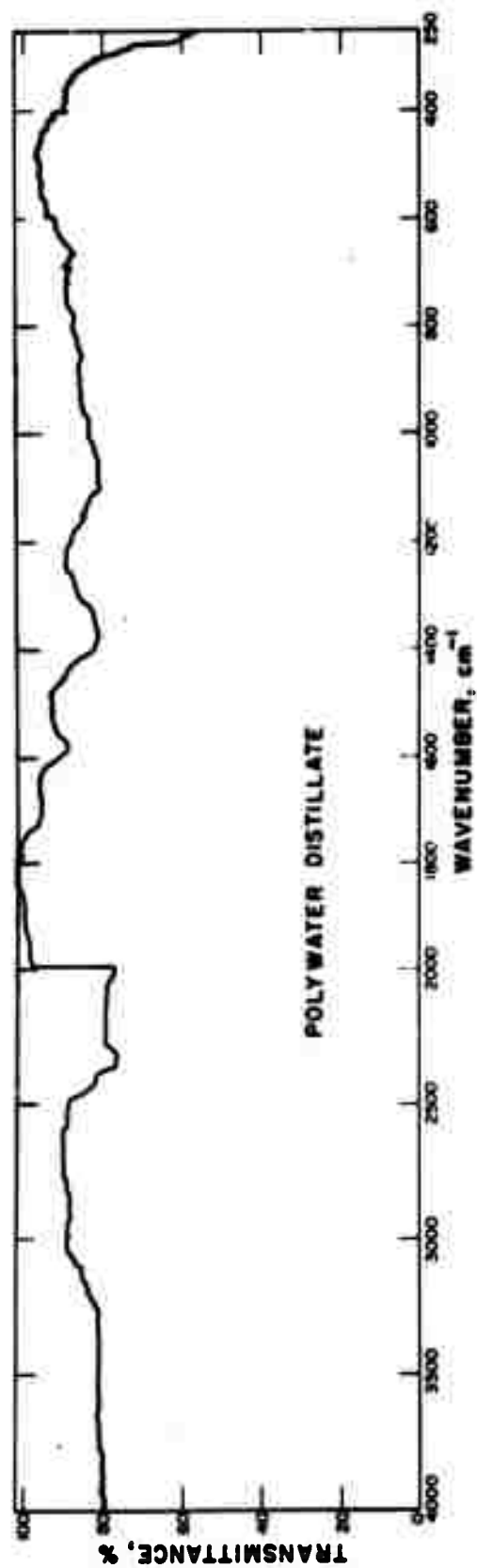


Fig. 16. IR spectrum of distillate No. 2

• Distillation No. 3: A third distillation was carried out with the same apparatus. The distillation chamber was baked at 200°C in the presence of O₂ for 4 hr, and the sample (about 200 µg) in a micro test tube was dried and heated at 250°C for 8 hr before use in order to eliminate organic materials. The sample was then placed in the distillation chamber, evacuated to less than 0.5 mm Hg pressure, and sealed. Then the sample was heated at 300°C. After 1 day, a crystalline product started to form at the tip of the cone. It took 5 days to complete the distillation. The chamber was opened and the product was exposed to water vapor. The distillate deliquesced and the solution was transferred to an AgBr plate for IR measurement. Although the IR absorption of this material is very weak, a band at 1650 cm⁻¹ and a broad band at 1250-1380 cm⁻¹ were observed. When this sample was acidified with dilute HCl and the IR scan repeated, the signal was considerably weakened, but no shift could be observed. This may have been due to volatilization or spreading of the sample on the AgBr plate; it does seem to indicate absence of carboxylic acids, however.

The residue of the distillation was also transferred to an AgBr plate for measurement. The IR spectrum of this residue shows strong absorption at 3200 to 3500 cm⁻¹, broad band at the 900 to 1400 cm⁻¹ region, and also absorptions at 700 and 1600 cm⁻¹. This spectrum suggests that the major portion is borate.

The difference between the second distillation and the third is that the sample of the latter was baked at 250°C in the presence of O₂ for 8 hr instead of at 200°C in air for 2 hr. The conditions for cleaning the sample are very vigorous and a good portion of the material was lost during this process.

• Distillation No. 4: This distillation was done with the same apparatus. The distillation chamber was baked at 200°C in O₂ for 4 hr. The pretreatment of the polywater sample, on the other hand, was altered quite drastically. It was felt that if there were salts of carboxylic acids present, then additions of acid would effect a conversion from salt to acid and result in volatilization of the material and thereby eliminate the organic constituents. Consequently, dilute HCl was added to the sample, which was then heated at 100°C for 4 hr. This process was repeated. Finally the sample was neutralized with NH₄OH and distilled, as before, at 300°C. The neutralization was to ensure that any borates would be present in the form of involatile salts and not distill. The fact that only a minute amount of distillate was obtained may attest to the fact that a major portion of the starting material was organic and lost as a result of the pretreatment.

• Distillation No. 5: The experimental procedure and sample treatment were identical to distillation No. 2, with the exception of sample size; this preparation was 500 μg of Pyrex-grown material. The distillation required 1 week to complete and yielded much more distillate than in all the previous experiments. An infrared spectrum was obtained which suggests the presence of both borates and organic material (Fig. 17). A spectrum was also obtained for the undistilled portion of the sample and is shown in Fig. 18. The bulk of this residue was not water soluble (probably carbon) and was separated out before running the IR analysis. One can see that the two spectra have a great deal in common, but they are far from identical. The main differences lie in a shift of the 1550 cm^{-1} peak of the residue to 1650 cm^{-1} in the distillate, plus the appearance of a peak at 1200 cm^{-1} in the distillate.

Due to the substantial yield of distillate (estimated at $\sim 25\text{ }\mu\text{g}$), it was possible to determine its molecular weight, which was found to be 262. Since tetraborate can be identified in the residue from the IR (c.f., Fig. 19), it is not surprising to observe a higher molecular weight for this distillate than for previous undistilled Pyrex-grown polywater samples (average weight = 183 ± 35). The molecular weight of a mixture determined by applying Raoult's law would be the algebraic average of all components, and, since the molecular weight observed by this method for $\text{Na}_2\text{B}_4\text{O}_7$ was 75, this implies that as much as 43% of the Pyrex-grown material is low molecular weight salt (expressed as $\text{Na}_2\text{B}_4\text{O}_7$).

After the completion of the molecular weight determination, distillate No. 5 was divided into two aliquots for a decomposition experiment. In the presence of a sufficient quantity of O_2 , organic material is most likely to decompose to H_2O and CO_2 at high temperatures. In absence of O_2 , it would probably crack or decompose to intermediate compounds (including a char and H_2O). Therefore, it was decided to compare the decomposition products obtained from aliquots of the same material by these two techniques.

The first aliquot was placed into a capillary and sealed under vacuum. The vacuum-sealed capillary was heated at 600°C for a period of 2 hr, with one end of the capillary remaining outside the heating unit to serve as a condenser. A small amount of yellow liquid was condensed at the cool end while a substantial quantity of black residue (probably carbon) formed at the original sample site. No attempt was made to obtain an infrared spectrum of this material because the sample was of insufficient quantity. Since the decomposition product was obviously not normal

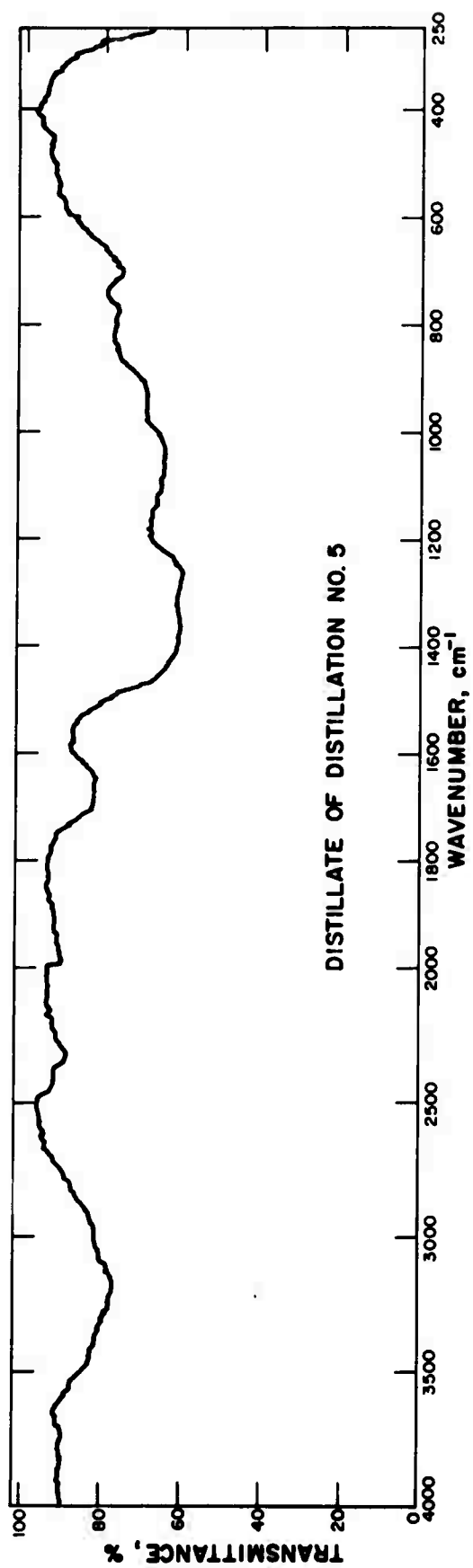


Fig. 17. IR spectrum of distillate No. 5

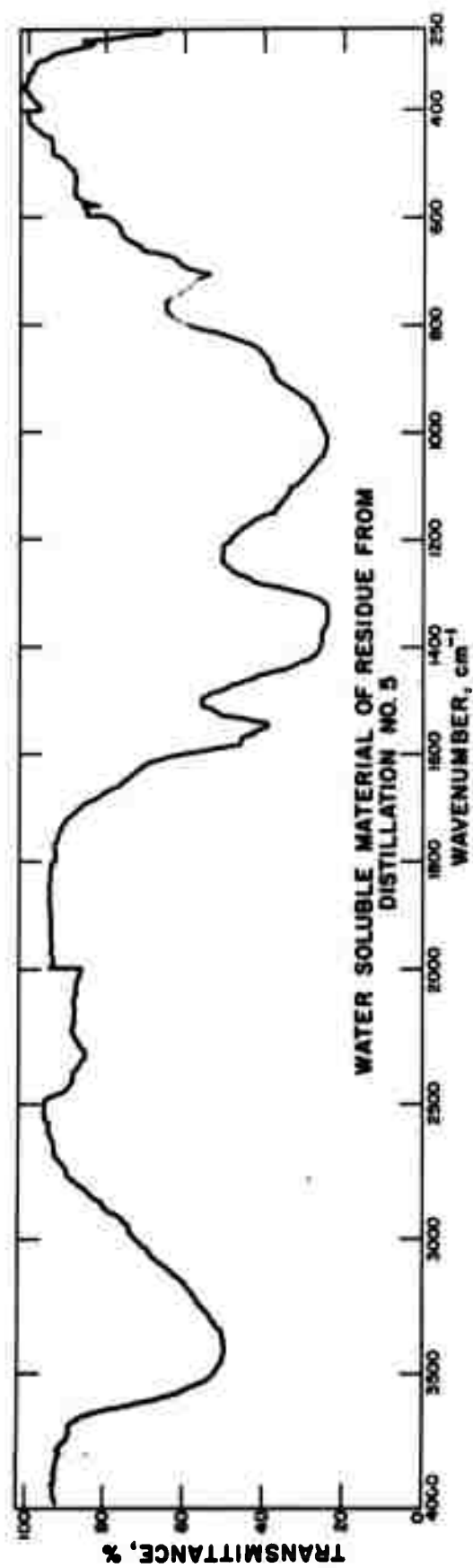


Fig. 18. IR spectrum of undistilled portion from distillation No. 5

water, a freezing point determination was not made. These results seem to indicate that the sample was partially organic. The infrared spectrum of the distillate suggested that borates may also be present.

The second aliquot was heated at 600°C for 2 hr, but in air. It was thereby hoped to decompose the sample into $\text{CO}_2 + \text{H}_2\text{O}$. A clear liquid formed at the cool end of the capillary which appeared to be H_2O . However, the liquid was found to freeze at -4°C which could mean that it contained some solute, e.g., borate. In addition to this liquid, some carbon was found on the walls of the capillary, similar to that found in the evacuated sample, although much smaller in quantity.

The general conclusions from these decomposition experiments are:

1. The particular distillate is predominantly organic in nature.
2. The decomposition is not quite the same as that for distillate No. 2 or to the Russian work, in that even in presence of air, H_2O is not the only visible product. We may note, however, that distillate No. 2, which was much smaller than distillate No. 5, was decomposed in the presence of a very large excess of air.

• Distillation No. 6: This experiment was performed on Pyrex-grown material which was air dried at 200°C for 2 hr prior to distillation at 300°C in vacuum. A yellow liquid condensed over. The condensate was then decomposed at 600°C in the same chamber. Part of the condensate carbonized and the rest of the sample condensed at the cool end of the chamber as a clear liquid (possibly H_2O). When this liquid was redistilled back to the carbon component, it turned yellow, probably as a result of extracting in completely decomposed material from the carbon layer. Fig. 19 shows the decomposition products. This yellow liquid displayed no IR activity.

• Distillation No 7: Zirconia-grown material was distilled as it may be the purest material of all, since absence of borates is assured, and the spectrum seems to show absence of SiO_2 . It was decided to distill the sample fractionally in 100°C increments in an attempt to separate any possible different components.

The first step of the distillation was carried out at 100°C. It produced first a clear and then a yellow liquid. The residue was removed and put into a new chamber, and then the experiment repeated at 200°C. A yellow distillate was also formed. The experiment at 300°C yielded the major product, which was dark yellow. This material appeared powdery, while the 200°C product seemed oily. The 400°C prod-



Fig. 19. The decomposition products from distillation No. 6

uct was a brownish powder distillate which was of much smaller volume than the other distillates, The residue became black during this experiment. At 500°C, very little distillate formed and the experiment was terminated.

Infrared analysis was then attempted on all the distillation fractions and on the residue. The 100°C fraction showed no IR activity and was probably composed mostly of water. The 200°C distillate was not water soluble, but when dissolved in a mixture of 75% EtOH and 25% H₂O, a weak diffuse spectrum was observed with no pronounced peaks. A slight dip in the region 1400 cm⁻¹ to 1600 cm⁻¹ was observed.

The 300°C product was dissolved in H₂O with difficulty and showed a well resolved spectrum (Fig. 20). The spectrum was relatable to, but distinctly different from, the spectrum of the original zirconia-formed sample (Fig. 21).

The 400°C and 500°C distillates were dissolved with difficulty in H₂O but displayed no IR activity, probably because of insufficient material.

As mentioned above, the residue turned black at 400°C. It was extracted with water to separate it from the insoluble carbon component. The spectrum shown in Fig. 22 revealed that it had strong ionic carbonate peaks at 1430 cm⁻¹ and 880 cm⁻¹. Since there were no carbonate peaks in the spectrum of the original zirconia-formed sample, the carbonate peaks in the residue prove conclusively that organic material must have been present in the original sample.

Additional strong peaks were evident at 1100 and 450 cm⁻¹. These correspond to the spectrum of SiO₂. While there was no evidence of SiO₂ in the original spectrum, it is not so surprising to find it in the residue. It merely means that silica constituted only a minor fraction of the total original sample and therefore could not be resolved in the IR. The major IR absorbers of this original sample were distilled, however, leaving the SiO₂ behind.

In an attempt to identify some of these stable organic components of anomalous water, the 300°C fraction was reserved for mass spectrometric analysis. The results of this experiment are discussed in the previous section.

D. Distillation of Sodium Tetraborate and Boric Acid

Since the presence of a tetraborate was positively identified by IR in the residue from polywater distillation No. 5, and strongly suggested in the distillate itself (refer to Figs. 17 and 18), it was decided to attempt a direct distillation of Na₂B₄O₇.

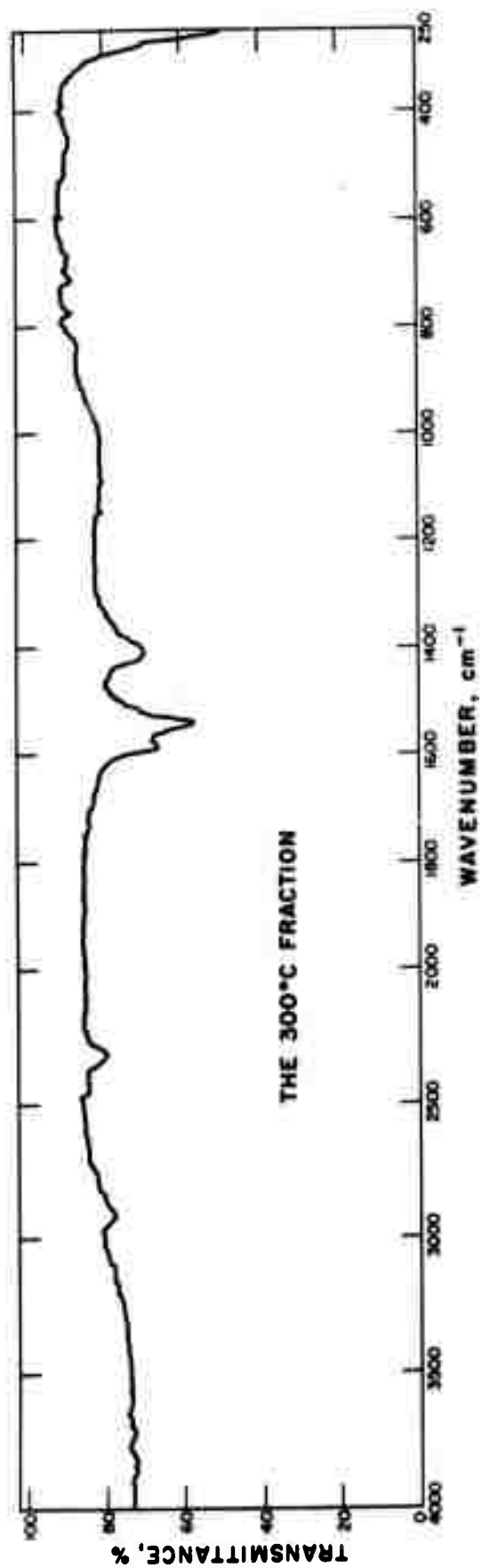


Fig. 20. IR spectrum of 300°C distillate fraction of zirconia-produced anomalous water

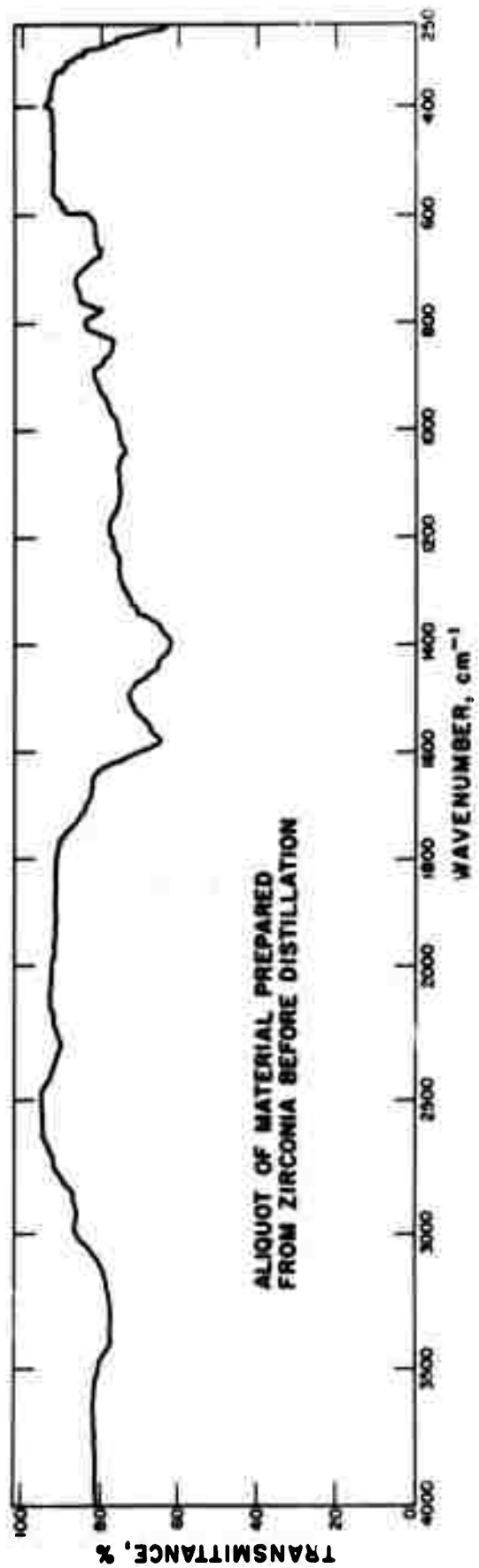


Fig. 21. IR spectrum of zirconia-produced anomalous water

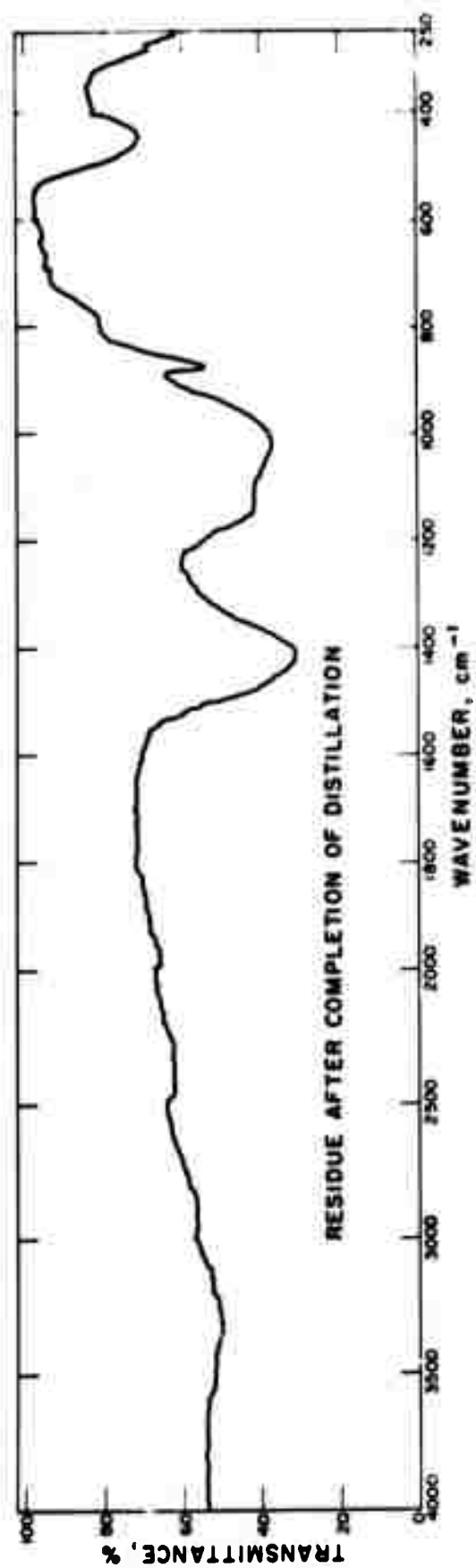


Fig. 22 IR spectrum of distillation residue of zirconia-produced material

Sodium tetraborate (Baker Analyzed Reagent grade) was placed in distillation chamber D (not under vacuum) and the heating unit was heated gradually. No product was observed at 100, 150, 200, 250, 300, and 450°C; only water condensation was found at the cool end of the tube. Then HCl was added to $\text{Na}_2\text{B}_4\text{O}_7$ to form H_3BO_3 . The IR spectrum of this boric acid is shown in Fig. 23. This material was successfully distilled at 150°C, and the infrared absorption of this distillate was identical to that of the starting material. An interesting feature of this spectrum is the absence of any absorption at 1000 cm^{-1} , which has always been observed for the tetraborate. The fact that boric acid distills and absorbs at 1400 cm^{-1} makes it not improbable that distillation product No. 5 does contain some of this material.

These two distillations were repeated under vacuum with essentially the same results; the tetraborate salt would not distill, and the boric acid distilled completely at the low temperature of 100°C.

E. Distillation of Poly-D₂O

We have already indicated that "poly-D₂O" and poly-H₂O" appear identical. Working on the assumption that the only material which could possibly be a polymer of water was the water-soluble distillate, an attempt was made to distill poly-D₂O with the aim of carrying out an IR-analysis of the distillate.

The sample for distillation was prepared from Pyrex cones suspended over a solution of D₂O under vacuum. All extracting and other handling were carried out in a glove bag continually flushed with dry N₂. The dried sample was evacuated, sealed, and distilled at 300°C.

The distillate was yellow and oily in appearance and proved to be insoluble in D₂O. This property made infrared analysis impractical since transferral of such a small quantity of material to an AgBr plate can only be accomplished by first dissolving the sample in hydrogen-free solvent.

Since the type of experiment which might be performed on this distillate was limited by the fact that the material would not dissolve in D₂O, it was decided to attempt a decomposition at 600°C in a vacuum. The results of this experiment were, predictably, much the same as in the case of the 300°C distillation. The major portion condensed at the cool end of the chamber as a dark yellow material which also proved to be insoluble in D₂O; a small amount of the sample remained behind and decomposed to a black char.

The evidence from these experiments indicates quite strongly that the sample is principally organic in nature.

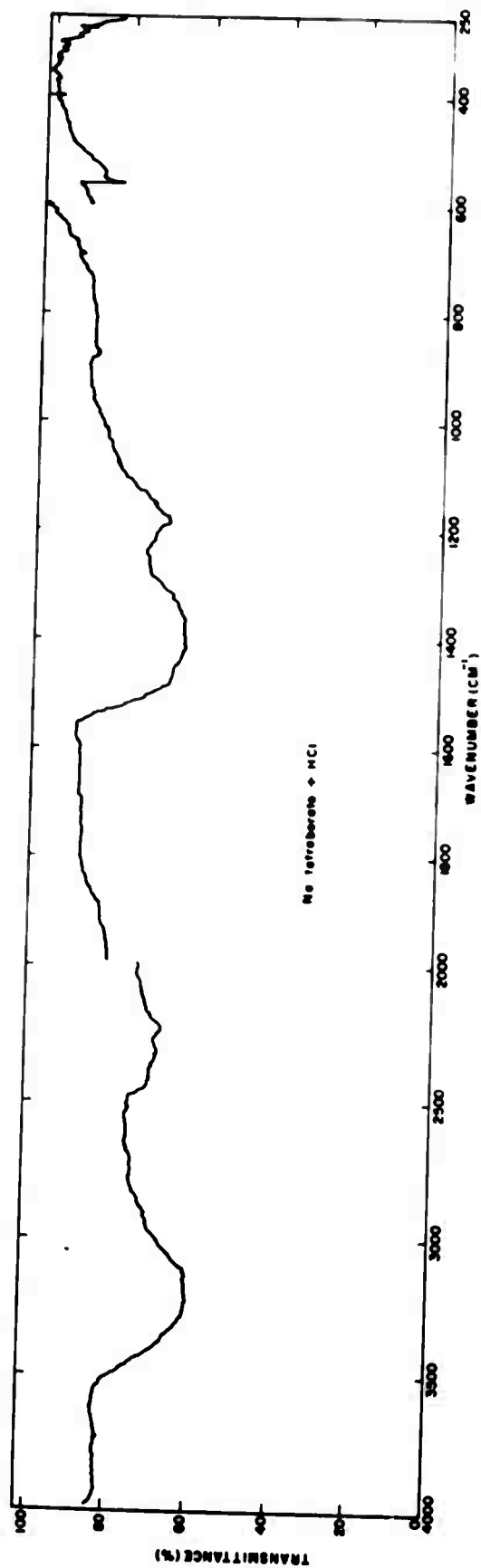


Fig. 23. IR spectrum of acidified $\text{Na}_2\text{B}_4\text{O}_7$

It will be recalled that the main purpose for undertaking this series of distillation experiments was to determine if, in fact, we are dealing with the same material as the Russians. From the above experiments, three general observations can be made:

1. Even though the distillation chambers were sealed under vacuum, distillation was never achieved below 300°C.
2. The yields were low, and there were considerable amounts of residue after the completion of all distillations.
3. In no case did a distillate decompose quantitatively to water.

These observations would appear to be in direct conflict with those of Deryagin, et al., who reported that polywater began to distill at 150°C, that the distillation was completed at 300°C, and that the material decomposed to normal water (usually with no residue) at 700°C. Therefore, an explanation was sought which might reconcile these differences in results.

Infrared analysis of distillates and their residues provided a great deal of information in this regard. In the case of the residue from Pyrex-grown material (ref Fig. 18), the IR spectrum revealed a high concentration of the 1600 cm^{-1} absorber which had failed to distill. Then too, one observes in the case of the distillate from this Pyrex-grown material (ref Fig. 17) that there was a distinct shift from 1600 to 1700 cm^{-1} in the IR. This spectral shift invariably connotes protonation of a carboxyl group to form the corresponding acid. Therefore, it was postulated that if the Russian material is also related to an organic acid, then our observations of higher distillation temperatures and high concentrations of organic residues could be the result of a systematic difference in the acidity of the preparations. In other words, for reasons related to the chemistry of the glass, the water, and the atmosphere, our preparations could be generally more alkaline than the Russian preparations.

One other point remained to be clarified: namely, the claim that their material decomposed to water at 700°C. In this regard, we have observed a notable difference in products, depending upon whether the decomposition was performed in the presence or absence of oxygen. That is, distillates which were subjected to a temperature of 600°C, under vacuum, would decompose primarily to carbon char with some yellow oils, not miscible with H_2O . However, in the presence of air, the decomposition products were primarily a clear liquid with a small amount of carbon

char. Since Deryagin, et al., did not perform their decompositions under vacuum, one cannot rule out the possibility that they were not observing the depolymerization of polywater but, in fact, the experiments were performed in the presence of sufficient quantities of oxygen so as to oxidize any carbonaceous material to CO_2 and water. Under these conditions, one can see the similarity between the two sets of results.

F. Acid Distillations and Boiling Point Determinations

In order to evaluate the theory that our higher boiling material resulted from a pH effect, polywater samples were distilled from acid.

A polywater sample was taken from the Pyrex 1-mg preparation and placed in a quartz micro test tube with 10-20 μl of $10^{-1} \text{ N H}_3\text{PO}_4$. Phosphoric acid was used because of its low volatility. The sample was evacuated to $<1\text{ mm Hg}$ and sealed. The capsule was then placed in a furnace at 100°C with one end of the capsule remaining outside the furnace to act as a condenser. White needlelike crystals immediately began to condense out. More condensation occurred when the temperature was raised to 150°C . Although the distillation was complete after 2 to 3 hr, the capsule was kept at 150°C overnight. Fig. 24 shows a picture of the distillate. The capsule was opened and the white crystals were dissolved in H_2O , siphoned into a fresh quartz microcone, evacuated, and sealed. The sample residue was yellow and viscous, with some dark material which was insoluble in H_2O . The H_2O soluble portion was siphoned into a fresh quartz capsule, evacuated, and sealed. This was returned to the furnace for additional distillation at 300°C . The sample charred, with no resulting distillate.

These preliminary results are different in many respects from the previous distillations. The first and most obvious difference is the lower temperature required. The fact that the reaction was completed in a few hours, rather than days, is also a notable difference. Finally, the yield, in terms of percent of starting material, was greater than in all the previous distillation experiments. This distillate was obviously more pure since it consisted only of the white crystalline material; this had not been the case in the previous experiments.

In order to determine the boiling point of this white crystalline distillate, the capsule containing it was placed entirely within a constant temperature zone of the furnace, along with a thermocouple (Fig. 25). The temperature at the capsule was raised slowly ($\sim 1^\circ\text{C}/\text{min}$), with continuous monitoring, starting at 100°C . The



Fig. 24. Product of the acid distillation of Pyrex-grown polywater (20X)



Fig. 25. Quartz capsule containing acid distillate in furnace. Dark circular area is thermocouple (20X)

capsule was also under constant microscopic observation, and the temperature at which the entire sample passed into the vapor phase was observed; there was no residue.

Prior to making the boiling point determination, the volumes of both the capsule and sample were calculated ($10.8 \times 10^{-2} \text{ cm}^3$ and $3.9 \times 10^{-5} \text{ cm}^3$). This made it possible to calculate the vapor pressure at the boiling point (226°C) for these conditions using:

$$P_1 = n \cdot R \cdot \frac{T_1}{T_2} \cdot \frac{P_2}{V} \quad (8)$$

Then, taking a density of 1.4 and a molecular weight of 260^* to calculate the number of moles of material present, we obtained a vapor pressure of 65.6 mm. This is extremely low compared to the Russian data, which reports a boiling point of $\sim 250^\circ\text{C}$ at 760 mm. This vapor pressure also appears somewhat unrealistic when compared to the distillation temperature. However, the measurement was then repeated after decreasing the capsule volume by nearly a factor of two, with no significant increase in boiling point. It was concluded that the ratio of capsule volume to sample volume was far in excess of the optimum ratio required for this measurement. Unfortunately, the rather large capsule diameter made any greater decreases in volume difficult to achieve.

An infrared spectrum of the distillate was obtained showing peaks at ~ 1700 , 1500, and 1100 cm^{-1} . Unfortunately, the spectrum was weak and poorly resolved, but it was possible to confirm the absence of peaks due to boric acid which absorbs at 1400 and 1200 cm^{-1} . Since this sample had been prepared on Pyrex, borate contamination had been suspected.

The possibility existed that the absorption at 1100 cm^{-1} may have been due to the presence of silicates or phosphates and not to the sample itself. Therefore, an acid distillation was performed on finely ground quartz using phosphoric acid. It was found that up to a temperature of 300°C , there was no distillate. While this confirms the applicability of the experimental technique, it does not account for the origin of the IR absorption observed at 1100 cm^{-1} in this distillate.

* This is the molecular weight determined experimentally using Raoult's law for a Pyrex polywater distillate (ref. this section, distillation No. 5).

The boiling point experiment was repeated using quartz-grown polywater. As in the case of the acid distillation of Pyrex-grown material, a white crystalline material distilled at 100-150°C from the sample, mixed with H_3PO_4 , and sealed under vacuum. The yield was also considerably greater than had been observed in normal distillations. This distillate was isolated in a quartz capsule of known volume and placed entirely within a constant temperature zone of the furnace with a thermocouple adjacent to the capsule. The boiling point was observed exactly as before and the vapor pressure determined from Eq. 8.

By decreasing the capsule volume between measurements, a series of boiling points at increasing pressures was obtained. Fig. 26 is a graph of the experimental data, plotted as $\log P$ versus $1/T$. The least-squares fit of this data gives an extrapolated boiling point, at 760 mm, of 355°C. This is to be compared with the value of 250°C reported by Deryagin, et al.²⁹

The latent heat of evaporation can be obtained from the slope of this graph by:

$$\frac{d (\ln P)}{d (1/T)} = \frac{\lambda}{R} \quad (9)$$

The value of λ from this expression is calculated to be 4.85 kcal/mole. This compares reasonably with the value of 6 ± 1 kcal/mole obtained by the Russians. The accuracy of our determinations is limited mainly by the sample volume measurements, which could only be made to within $\pm 10\%$ due to their irregular shape in the capsule. Nevertheless, it has been shown that it is possible to isolate a more volatile species from our quartz-grown polywater, with properties rather similar to those reported by Deryagin, et al.

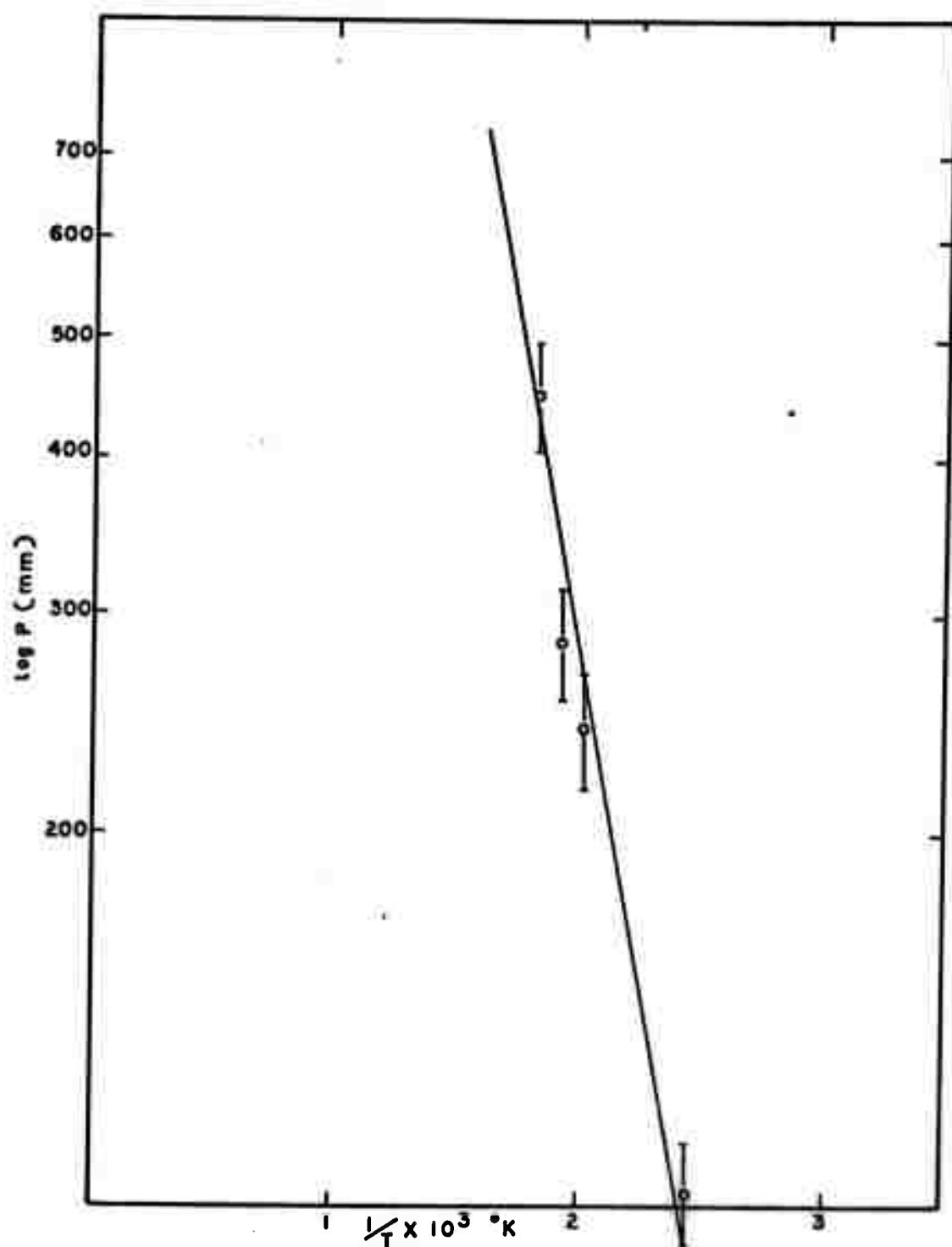


Fig. 26. Temperature dependence of saturated vapor pressure of quartz-grown polywater

V. SUMMARY AND CONCLUSIONS

A major achievement of the present work has been to systematize the preparation of anomalous water. Thus, the cone technique has been developed to the point of reliably producing an approximate monolayer of material. Considerable experimentation has shown that this technique involves the optimum method of preparation and that it would not be easy to prepare large areas of glass so as to enhance the overall amount of the product by any substantial amount. In this section we intend to summarize our views on the following questions about this cone-produced material:

1. Is the material the same as other U.S.-grown polywater?
2. Is the material the same as the "water-II" of the Russian workers?
3. What is the nature of the material?
4. What is the origin of anomalous water?

1. Is the material the same as other U.S.-grown polywater?

The main evidence on this point involves the IR spectra. The IR spectra that we have reported suggest, as we shall discuss below, that polywater, as prepared, may comprise a mixture of organic and inorganic compounds. In other words, there is a range of infrared spectra depending on the mode of preparation and the substrate. Nevertheless, we may say that almost all of our samples do contain the characteristic polywater peaks reported originally by Lippincott, et al.¹³ and observed by Rousseau et al.¹⁴ and by many others, i.e., the fairly sharp peak around 1600 cm^{-1} , the broad peak – sometimes a doublet – between 1410 and 1350 cm^{-1} , and the broad peak around 1100 cm^{-1} . Typically, this sequence is also the order of decreasing band intensity.

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The refractive index data are also relevant here. To our knowledge only Lippincott, et al.,¹³ and Castellion, et al.,¹² have reported on the refractive index of their material, and in both cases the measured values were in close agreement with Deryagin's value⁵ and with our own.

There can be little doubt, then, that the material prepared in our laboratory is identical to that prepared in other laboratories in this country and characterized substantially by its infrared spectrum.

2. Is the material the same as the "water-II" of the Russian workers?

This is the crucial question. If there is any residual doubt that these may be a polymer of water, it results from the experiments carried out by the Russian workers. In particular, we may note:

- a. their preparation of material under apparently organic-free conditions;
- b. their ability to distill the material without change and subsequently, under extreme conditions of heating, to decompose it – apparently back to pure water.

We shall attempt to answer the question by systematically comparing the data on molecular weight, refractive index, general thermal stability, and distillation, and we shall direct a special challenge to their so-called "organic-free" preparation.

The molecular weights of our material under identical conditions (96% relative humidity) to theirs are 193 ± 25 for quartz-grown material and $166 \pm 45^*$ for Pyrex-grown material. This is to be compared with their value of 180 ± 50 for quartz-grown material.⁶ We may note that the actual values of the molecular weight so obtained are in moderately good agreement with the value determined in the mass spectrometer, and this finding tends to validate the meaningfulness of the data. In our view there can be little doubt that within sensible limits the molecular weight determinations do indeed indicate that we are dealing with the same material as the Russians.

*These values, for reasons discussed elsewhere,²⁴ are not the best true values of the molecular weight, but they are the most suitable for comparison with the Russian work.

A similar conclusion seems appropriate in connection with the refractive index data. Thus, they have reported 1.49 ± 0.01 for quartz-grown material, whereas we find 1.53 ± 0.04 .

The thermal stability – decomposition – boiling point data are more complex. There can be little doubt that our material substantially reproduces the general thermal stability and low volatility reported by the Russians, but there are differences and, for example, our material tends to be somewhat less volatile than theirs. Thus, they report a normal boiling point of about 250°C , whereas we find that as-prepared material appears to distill only slowly in vacuum at 300°C . We believe that there are two reasons why our material appears less volatile in this way. Firstly, much of our work has been done with Pyrex-grown material, and there is often considerable contamination of it with involatile inorganic material. Secondly, the major component which as we shall discuss below, we believe to be organic, substantially does not distill unless the overall material is acidic. It seems to us that the substantial effect in our 300°C vacuum distillations is one of decomposition plus hydrolysis. This hydrolysis, we believe, forms a small amount of an acid product which can distill relatively readily. This conclusion is substantiated by the shifts in the IR spectra seen on acidification and by the very much readier volatility of our material when it is acidified. Even so, the boiling point of our acidified product is quite distinctly higher than that reported by the Russians. In our view, this difference probably may reflect a small variation in molecular structure, albeit that the overall molecular weight is rather similar. Also, there may be enough uncertainty between both boiling point determinations to suggest that there is no substantive difference between the materials.

The general reason why our materials prior to acidification do not distill as readily as theirs would have to be explained, we believe, by assuming a difference in acidity between the preparative techniques used in the respective laboratories. In some experiments they do report residues left after distillation. These may result from variations in acidity or from adventitious inorganic contamination.

Item (b), listed previously, indicating that their material decomposes only to water (also, we may note, leaving an occasional residue), has been substantially reproduced in our laboratory provided an excess of air is present in the decomposition chamber. The exact conditions in the Russian work are not spelled out, but certainly the volumes of capillary they used were large in comparison with the volumes of

material decomposed. Therefore, if the capillaries were not evacuated, there would have been a large excess of air present. Correspondingly, the only visible observable product should have been pure water, as they reported.

Next in this regard, we must consider their so-called "organic-free" preparation. Our results show clearly that the organic material produced on the surface of hot glass in the presence of organic contaminants in the atmosphere can survive the high-temperature evacuation procedures to which they subjected their glassware after preparation of the capillaries. Consequently, we have no doubt whatsoever that there is no substance to their claim of "organic-free" preparation. We have little doubt, then, that our major material, which we shall discuss below, is predominantly organic in nature and is equivalent to their major material.

3. What is the nature of the material?

We believe that the major component of our material, and presumably also of Deryagin's, is organic in nature, although there are frequently inorganic contaminants.

That the major component of our material is organic can be inferred from the following data. Firstly, the main infrared peaks at 1600 and between 1350 and 1400 cm^{-1} do correspond, among other things, to typical carboxylic acid salts. This view is substantiated by the behavior of the infrared peaks on acidification. In particular, we note that the 1600 cm^{-1} peak tends to shift to 1700 cm^{-1} or slightly higher, typical of a carboxylate acid shift. The infrared spectra also provide other evidence for presence of organics, e.g., the C-H stretch just below 3000 cm^{-1} which is often found, and the $\text{CO}_3^{=}$ bands often found after heating the material.

The effects of heating also provide evidence in that samples, especially when heated in vacuum, almost invariably show some charring. Also, strong heating in presence of excess air apparently leads to the formation of H_2O as the only visible product. It appears certain from all our studies that these results relate to the major constituent of our material and that, therefore, the material is predominantly organic in character. Aside from the specific information about its properties reported above, we do not know the identity of the compound.

There have been a large number of suggestions that anomalous water comprises substantially inorganic constituents which are leached out of the apparatus or from the glass preparation tubes. Various, it has been claimed that anomalous

water is a silica sol or gel, a $\text{SiO}_2\text{-HCO}_3^-$ agglomerate, $\text{B}_4\text{O}_7^{=}$ extract from the glass, an organo-silicon compound, or a volatile hydrated silica.

As we have indicated, there is often evidence in many of the Pyrex preparations for presence of $\text{B}_4\text{O}_7^{=}$. This is not typical of the material, however, when it is grown on quartz or on ZrO_2 -based glass. Even with Pyrex, borate is only a minor constituent of our material.

The evidence on SiO_2 is that many examples do show IR peaks corresponding to silica (i.e., a broad band around 1100 cm^{-1} and peaks at around 800 and 450 cm^{-1}). This is not typically the predominant influence, however, and while we do believe that some silica is often leached from the glass into the sample, it certainly is not a necessary contaminant even for quartz-grown samples. For example, in our experiment where we pulled quartz cones in purified O_2 and baked them in vacuum, almost no product was obtained – certainly too little for an IR spectrum. The ZrO_2 -based glass material did not show the 1100 cm^{-1} band and, generally, we believe that presence of this band is mostly indicative of the silica content of the material.

The overall conclusion on the composition of anomalous water is that it is substantially organic, that this organic behaves like a hydrolyzable derivative of a carboxylic acid, and that it is sometimes contaminated with inorganic species which can lower its molecular weight and can contribute side bands to its infrared spectrum. Based on all the available evidence, including the spectral studies of polyheavywater, we would conclude that polywater is not a polymer of water.

4. What is the origin of anomalous water?

The experiment with cones drawn in presence of purified O_2 shows conclusively that anomalous water is formed during the glass blowing process itself by reaction with an organic species in the atmosphere. A significant question relates to exactly which kind of organic contaminant is responsible for this reaction. Rousseau, et al.,^{18,19} have suggested that the material is formed from a decomposition product of human sweat. Gardiner, et al.,³⁴ have shown that the infrared spectrum of polywater can be approximately reproduced by heating sodium lactate, the infrared active component of sweat. They suggested that products left on the glass as a result of handling it would be decomposed during glass blowing and would therefore be responsible for the "polywater" subsequently found.

Our own data strongly disagree with this latter specific origin and, rather, indicate that the organic material is deposited on the glass via the atmosphere. We too find a reasonable similarity between the small water-soluble residue of charred sweat and polywater, at least so far as their infrared spectra are concerned. The distillation properties are quite different, however, since charred sweat leads to a yellow water-immiscible oil, while polywater usually gives a colorless water-soluble product. It is possible that this latter property results from inorganic contamination in the case of the polywater samples, e.g., in some cases with borate and perhaps fairly generally with a small amount of silica. The latter, we believe, is responsible for the broad 1100 cm^{-1} absorption band. It may be significant in this regard that the sample produced on ZrO_2 -based glass, which did not show the 1100 cm^{-1} band, gave a distillation product which was difficult to dissolve in water.

In conclusion, then, it would appear that the sweat theory of polywater is at least a good approximation. Apparently it is not possible to heat glass in the atmosphere without producing about a monolayer of an organic compound on its surface. This material may be more or less contaminated with inorganic constituents, but they are of minor significance. The evidence is overwhelming that this material is the same as the "water-II" of Deryagin. We conclude, therefore, that neither he nor they have been studying a polymer of water.

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